Mapping Plasmons, Structure, and Composition in Complex Bimetallic Nanostructures

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Assistant Professor of Chemistry

ASCI
Boise State, May 18th 2016

Materials Science and NanoEngineering @ Rice

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Senior Faculty Fellow

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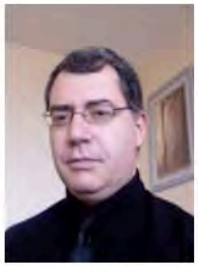
Distinguished Faculty Fellow in Chemistry and Materials Science and NanoEngineering



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Executive Director of Rice Quantum Institute, Faculty Fellow in Materials Science and NanoEngineering

Robert Vajtai
Senior Faculty Fellow

Established 2013 from MEMS

Ringe Group, Est. 2014

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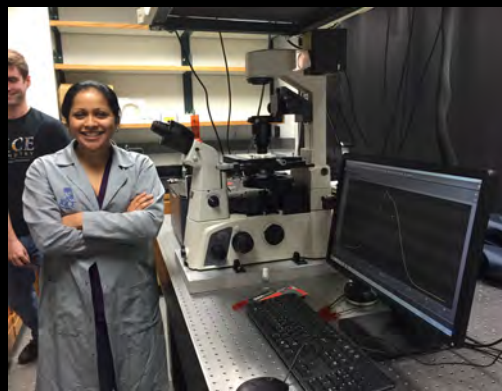


Rice EM Center

FEI Helios NanoLab 660
Scanning electron microscope/Focused ion beam (SEM/FIB)

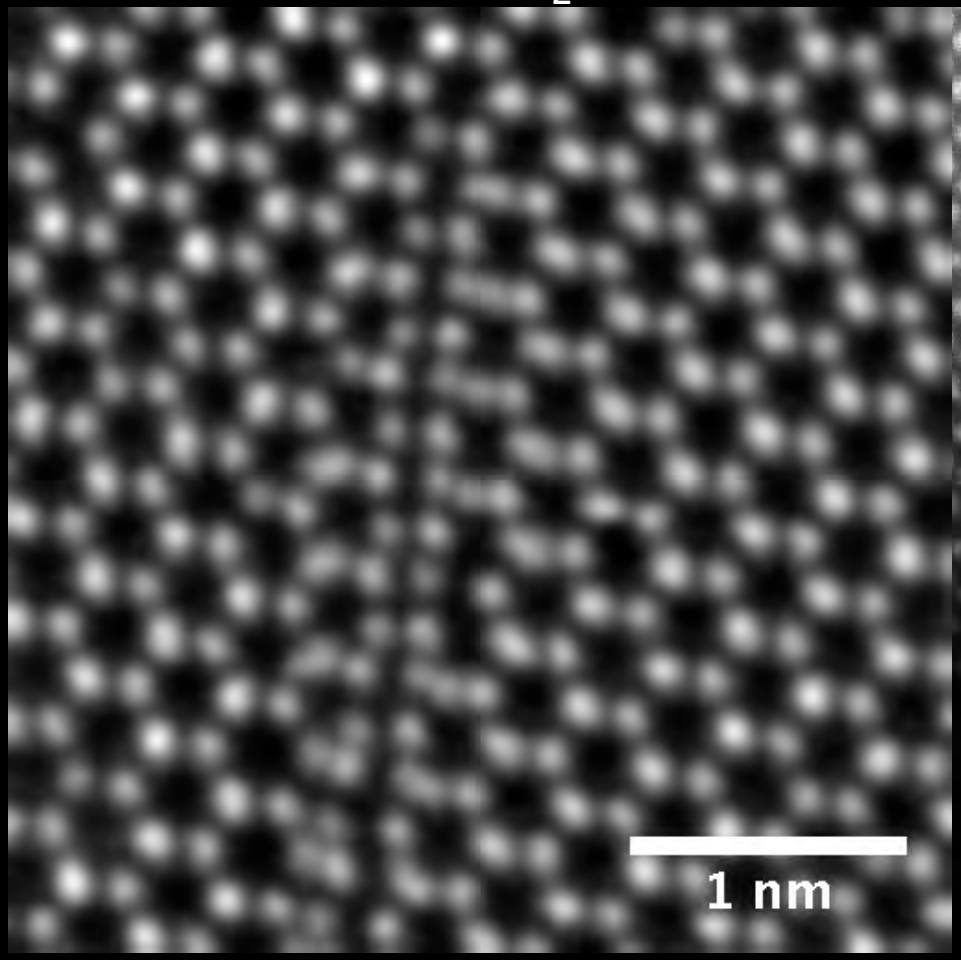
- Sub-nm resolution achievable 0.5-30 kV
- SEM voltage tunable from 20 V - 30 kV to suit the needs of all users, from biologists to engineers
- FIB with Ga ions 0.5 kV - 30 kV for fast cutting and damage polishing
- Easylift EX manipulator for sample transfer
- AutoSlice and View 3D reconstructions for visualization of large specimens
- Secondary electron and 2 backscattered electron detectors

FEI Titan Themis^3 300
Scanning Transmission Electron Microscope (S/TEM)

- Operates in TEM and STEM mode
- Image+probe correctors for sub-A resolution
- Ultra-bright XFEG gun
- Voltage tunable 60-300 kV, suitable for beam-sensitive samples
- Monochromator, ZLP FWHM <0.2 eV for EELS
- High speed Gatan Imaging filter for large scale spectrum imaging and energy-filtered imaging
- High tilt holder for tomography
- Cathodoluminescence holder
- 4K X 4K CMOS camera for fast large area imaging
- Super-X quad EDS detector for elemental analysis
- HAADF and triple DF/BF detectors for simultaneous imaging in STEM mode

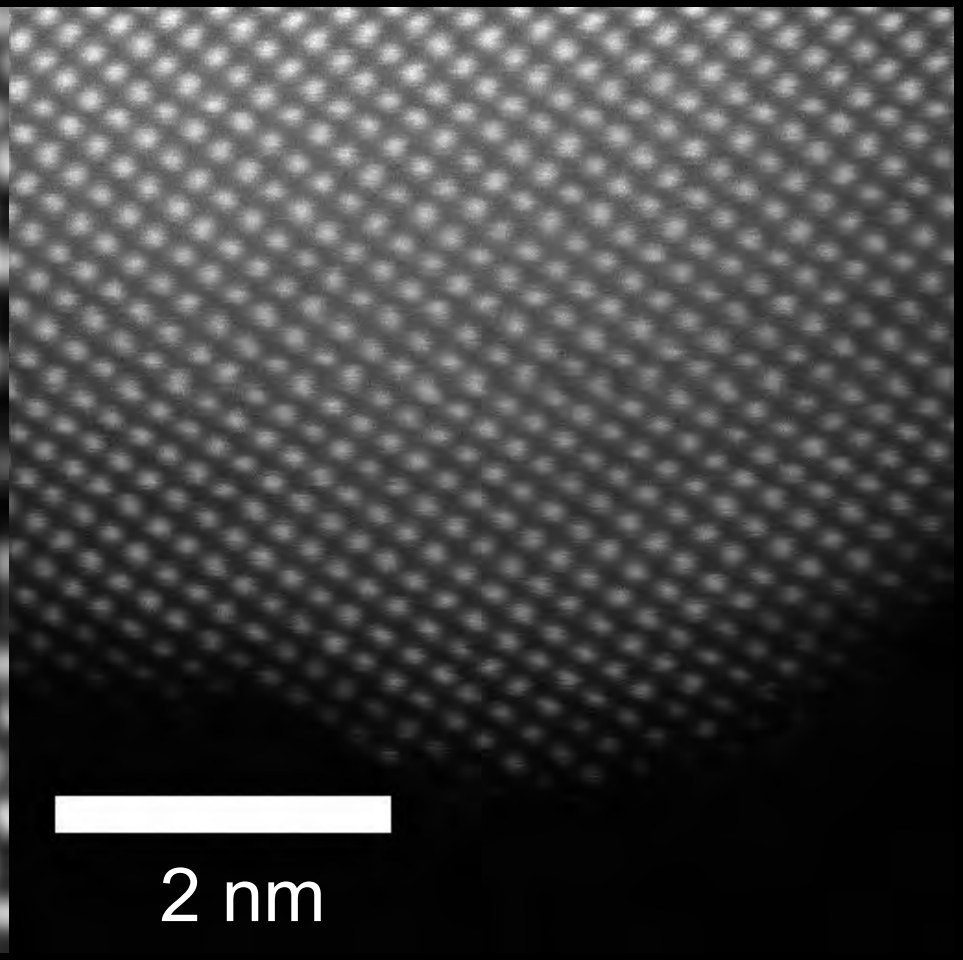
Atomic Resolution Imaging

$MoSe_2$



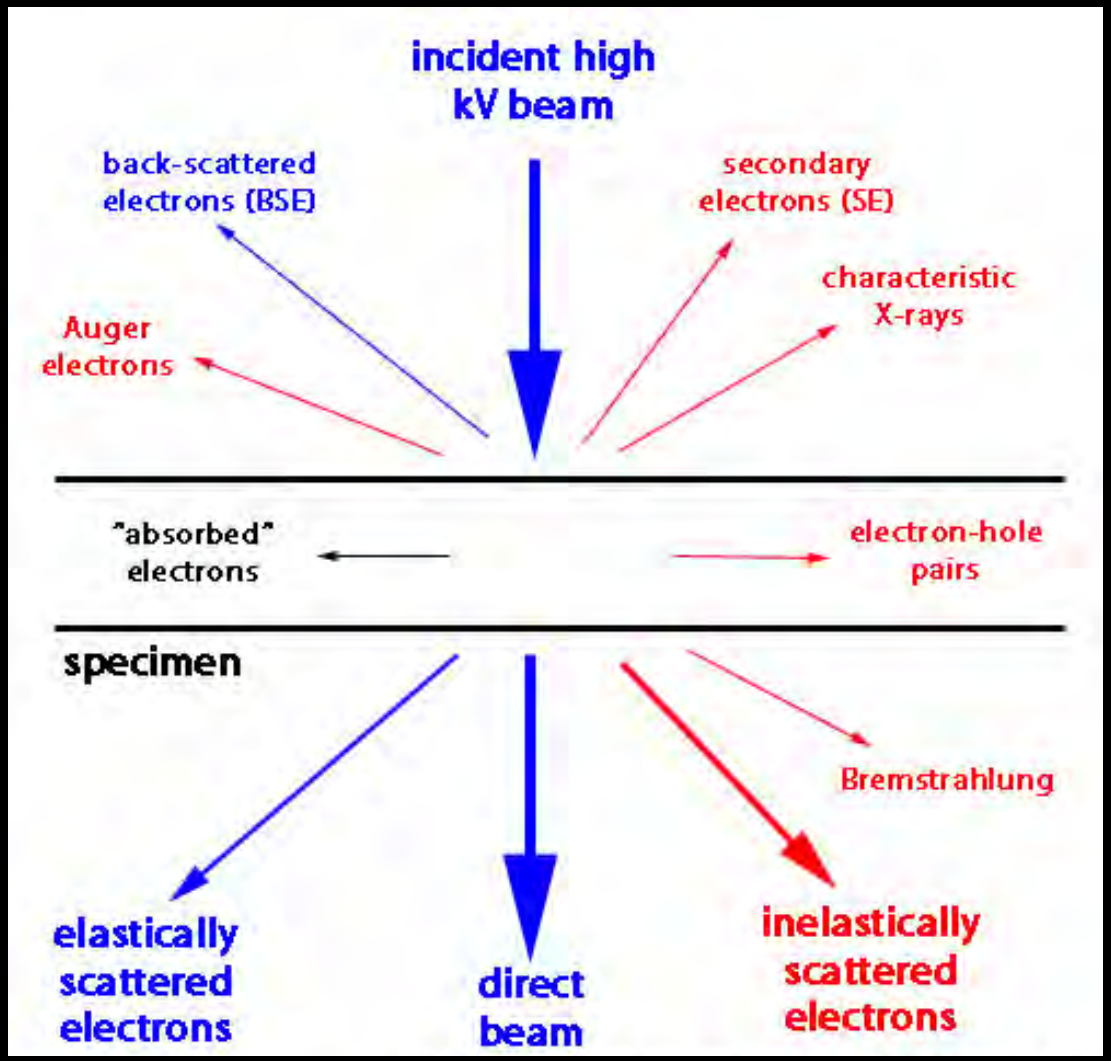
X. Wang, Y. Gong, G. Shi, W. L. Chow, K. Keyshar, G. Ye, R. Vajtai, J. Lou, Z. Liu, E. Ringe, B. K. Tay, and P. M. Ajayan, ACS Nano (2014), 8, 5125-5131

Au/Pd



E. Ringe, C. J. DeSantis, S. M. Collins, M. Duchamp, S. E. Skrabalak, and P. A. Midgley, Sci. Rep. (2015), 5, 17431

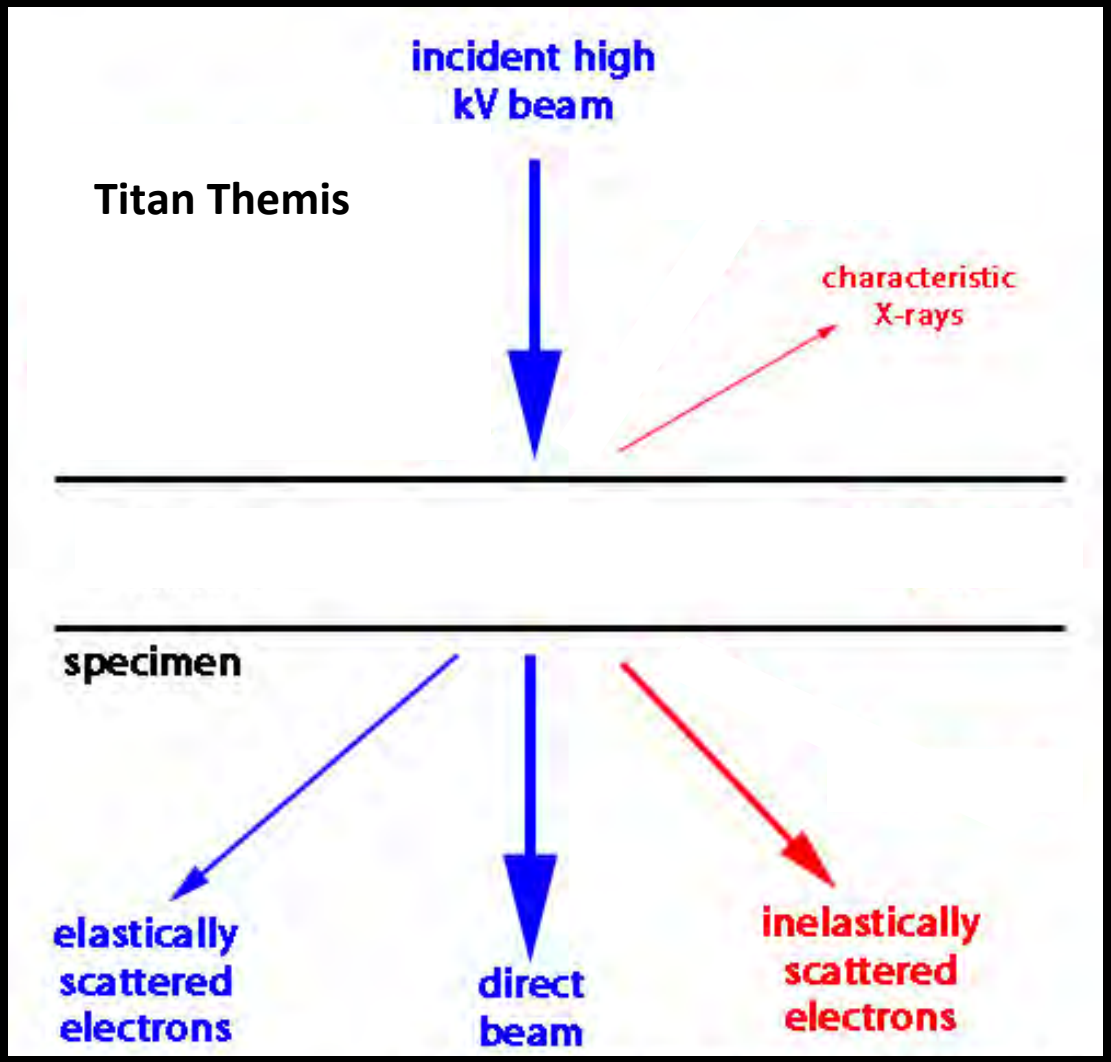
Signals in Electron Microscopy



Plus different modes:
Tomography
Diffraction

Adapted from Williams & Carter (1996) fig. 1.3
Red = energy change. Blue = same energy

Signals in Electron Microscopy

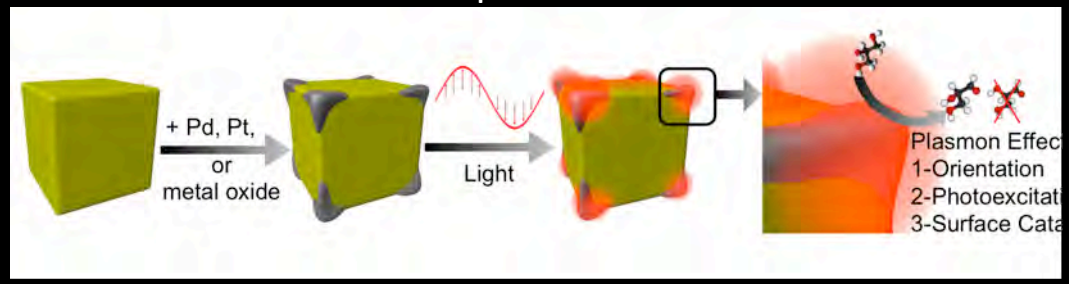


Plus different modes:
Tomography
Diffraction

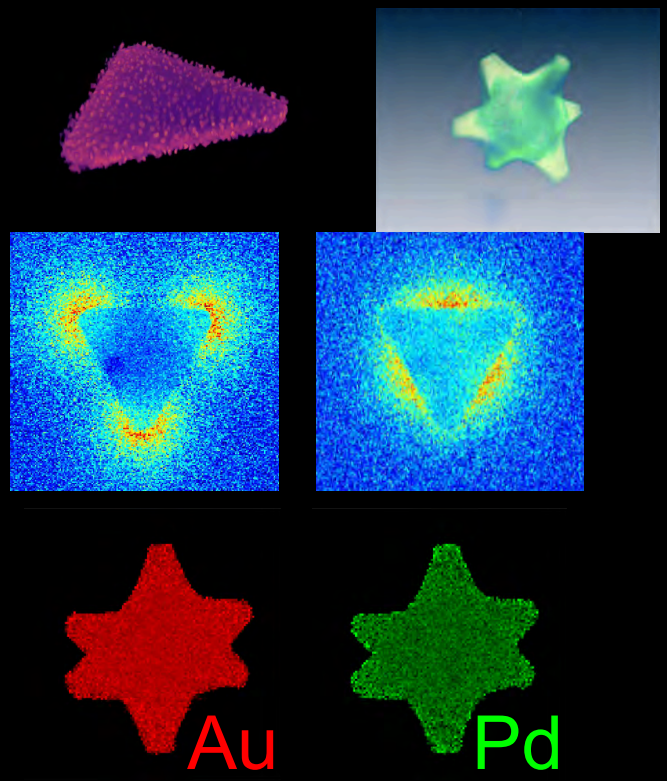
Adapted from Williams & Carter (1996) fig. 1.3
Red = energy change. Blue = same energy

Research Goals

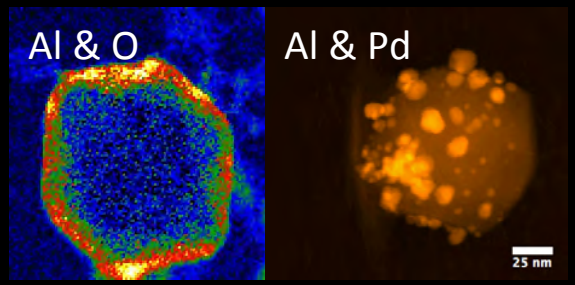
Plasmon field manipulation of chemical reactions



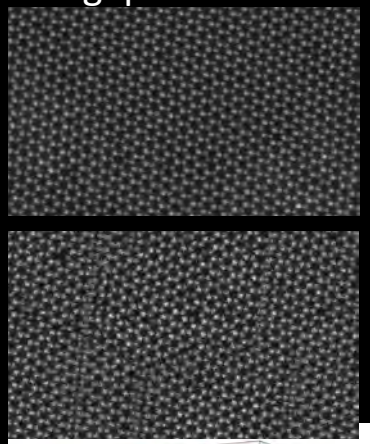
Bimetallic nanostructures:
catalysis + plasmonics

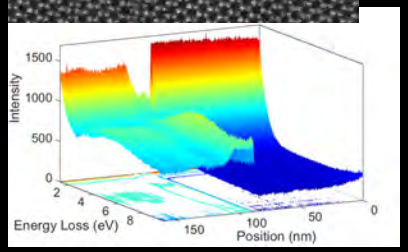


New plasmonic Materials

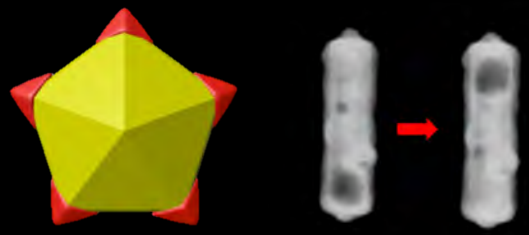


2D materials
bandgap & defects



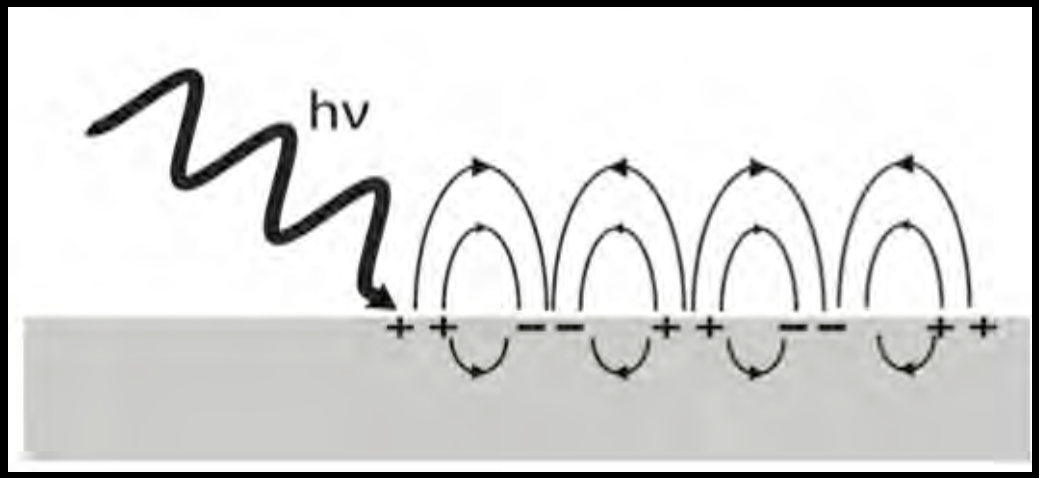


Reprogrammable & reconfigurable
plasmonics & catalysts

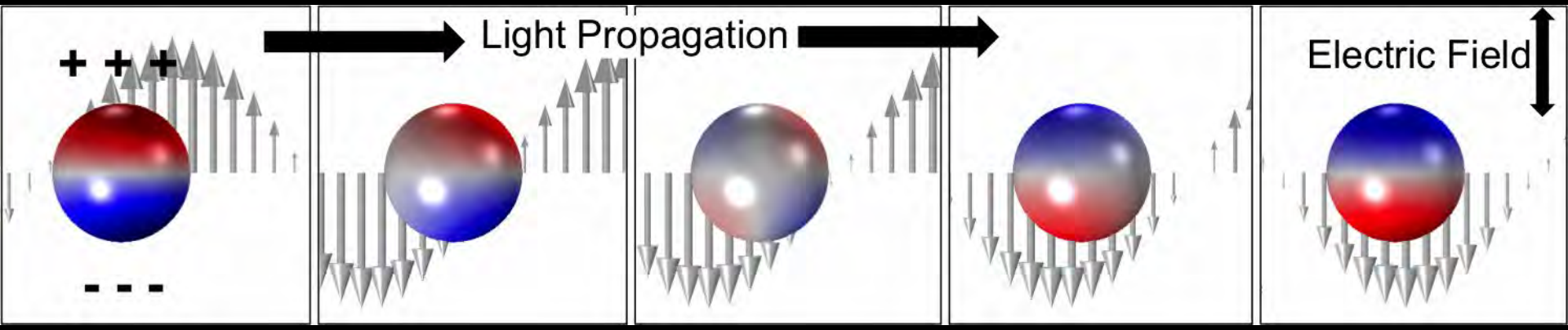


Surface Plasmons

Propagating surface plasmon
- Charge oscillation travelling at metal-dielectric
- Field decay length ~200nm
- High refractive index sensitivity but bulk sensing

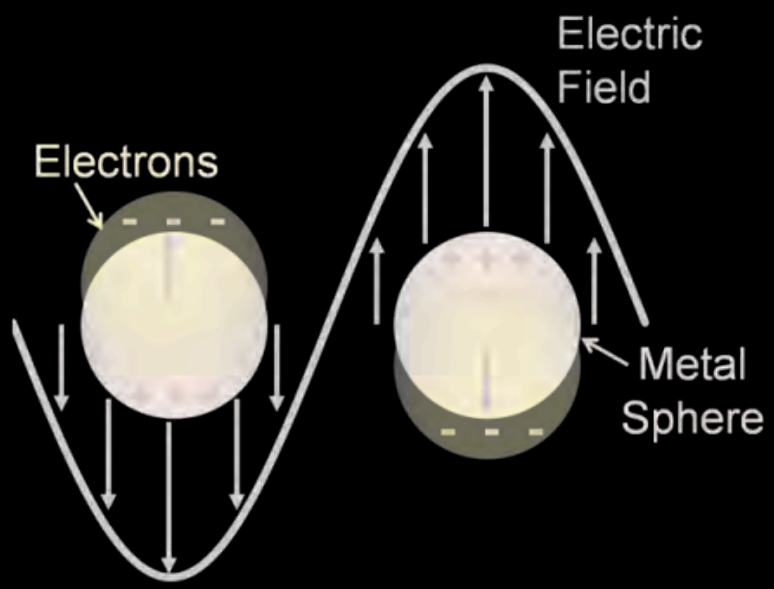


Localized surface plasmon resonances (LSPRs)
- **Localized** charge oscillation
- Narrow resonance
- **Short field decay length** 10s of nm



Metal Nanoparticles Sustain Plasmon Resonances

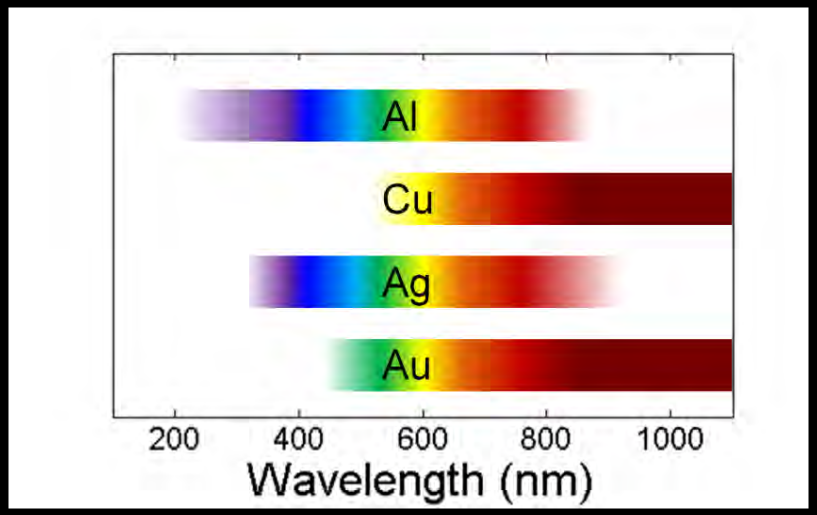
Localized Surface Plasmon Resonance



Plasmon periodic table, blue sustain LSPR

Li 0.14* 28.82	Be 0.20 3.58		Element Frequency of Max QLSP Maximum QLSP										B	C	Max Qlsp Key 0.00-2.99 3.00-3.99
Na 1.44 35.09	Mg 4.00 9.94												Al 11.00 13.58	Si	4.00-6.99 7.00-9.99 10+
K 1.05 40.68	Ca 0.65* 3.63	Sc 0.3* 1.02	Ti 0.20 2.58	V 0.36 4.27	Cr 0.30 2.16	Mn 0.07* 1.16	Fe 0.10* 2.48	Co 0.10* 2.69	Ni 0.15 2.71	Cu 1.75 10.09	Zn 3.60# 3.59	Ga 8.30 3.41	Ge	As	Se
Rb 0.81 21.90	Sr 0.36* 2.85	Y 1.48* 1.41	Zr 3.00 1.16	Nb 0.55 3.39	Mo 0.38 5.38	Tc	Ru 0.10* 2.03	Rh 0.30 2.10	Pd 0.10* 6.52	Ag 1.14 97.43	Cd 0.65# 3.63	In 5.10 4.60	Sn 2.25 3.50	Sb 3.50 1.33	Te
Cs 0.51* 11.20	Ba 1.91 0.91	Lan	Hf 0.52* 0.79	Ta 0.58 5.25	W 0.30 4.96	Re 0.10* 4.99	Os 0.10* 6.12	Ir 0.40 2.55	Pt 0.35 1.96	Au 1.40 33.99	Hg 4.20 2.20	Tl 3.20 2.71	Pb 5.95 3.07	Bi 3.50 1.15	Po

* wmax is at the limit of the available data
# low requency data not included



Accessible LSPR Range depends on plasma frequency & electronic transitions

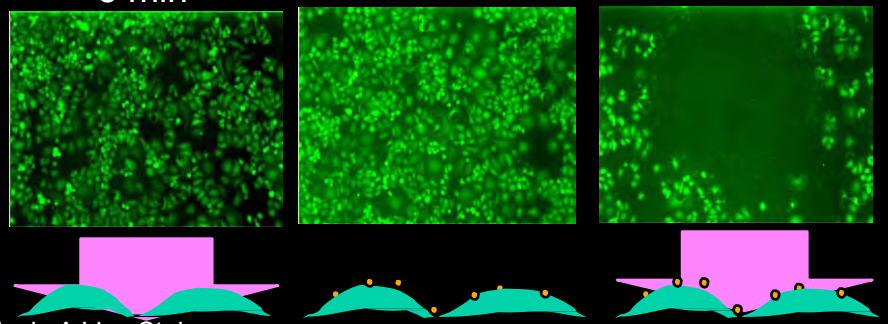
For a given metal, size, shape & surroundings control the LSPR

Not all metals are plasmonic

Sensing, Spectroscopy, and Catalysis: Plasmonics Application Examples

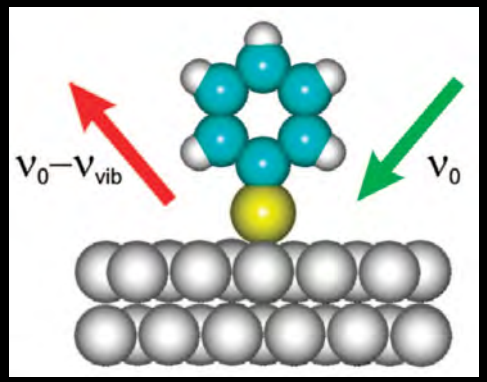
Absorption → Localized Heat

No nanoshells 5 min | Nanoshells 0 min | Nanoshells 5 min

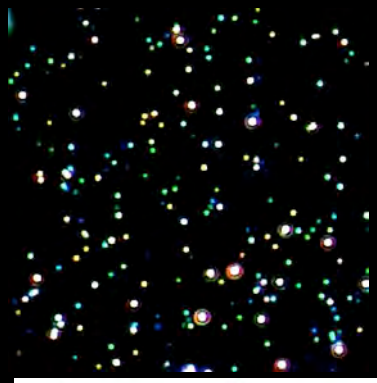


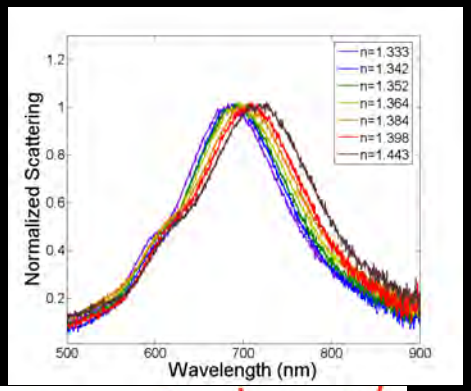
Calcein A Live Stain

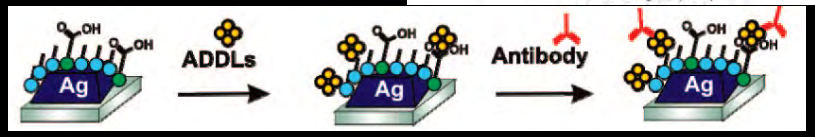
Enhancement of the Local EM Field → Surface-Enhanced Spectroscopies



Scattering & Absorption → Sensing





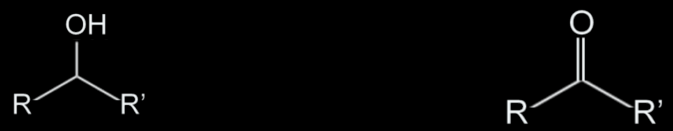


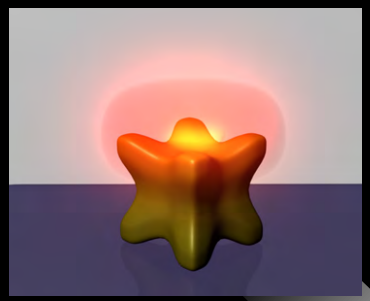
L. R. Hirsch, R. J. Stafford, J. A. Bankson, S. R. Sershen, R. E. Price, J. D. Hazle, N. J. Halas, J. L. West, PNAS (2003) 100, 13549

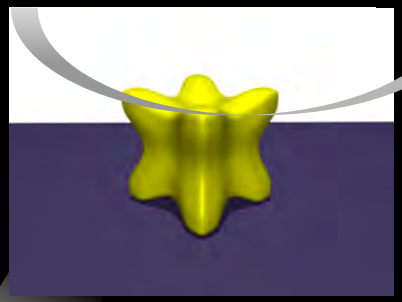
A. J. Haes, L. Chang, W. L. Klein, R. P. Van Duyne, JACS (2005) 127, 2264

Catalysts →
Favorable Surface Chemistry

Absorption →
Hot Electrons & Fields for Photocatalysis



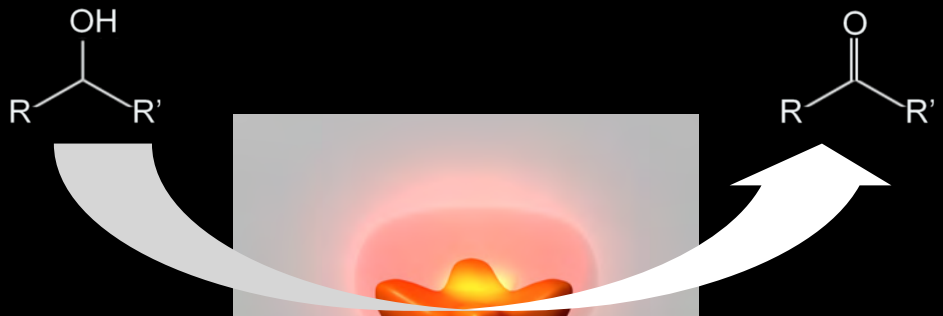


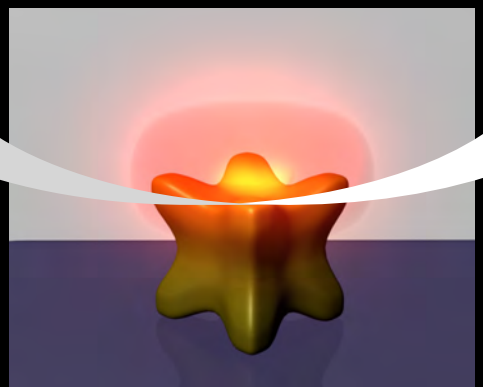


Au, Ag, Cu, Al

Pd, Pt

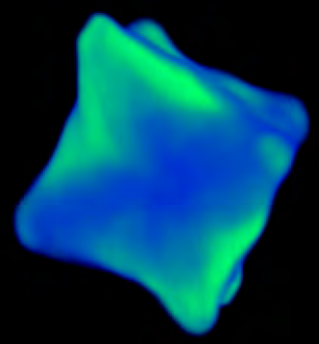
Photocatalysis / Plasmon-enhanced catalysis





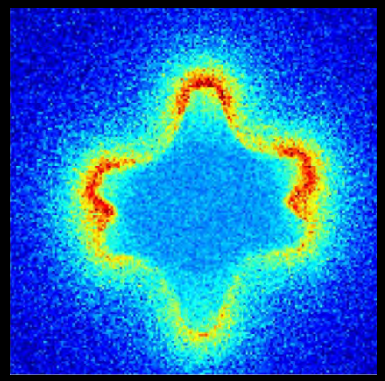
Combining Plasmonics and Catalysts: 2 Recent Examples

Au/Pd Octopods

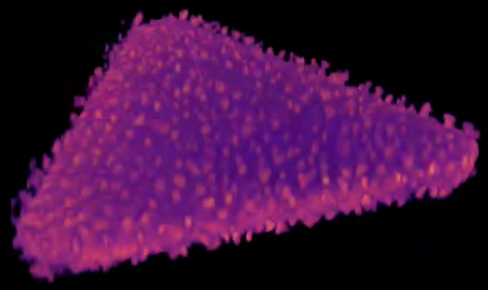


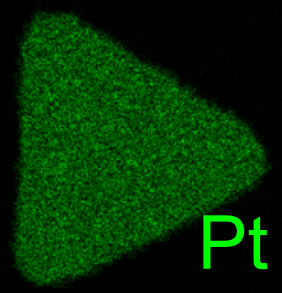
Pd

Au

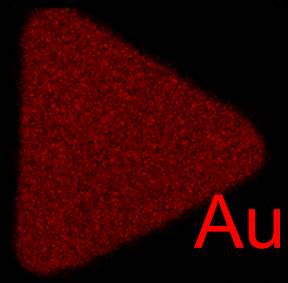


Au/Pt Prisms

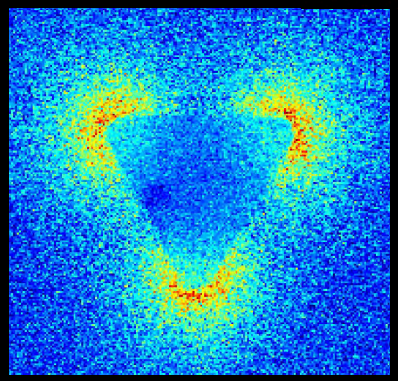




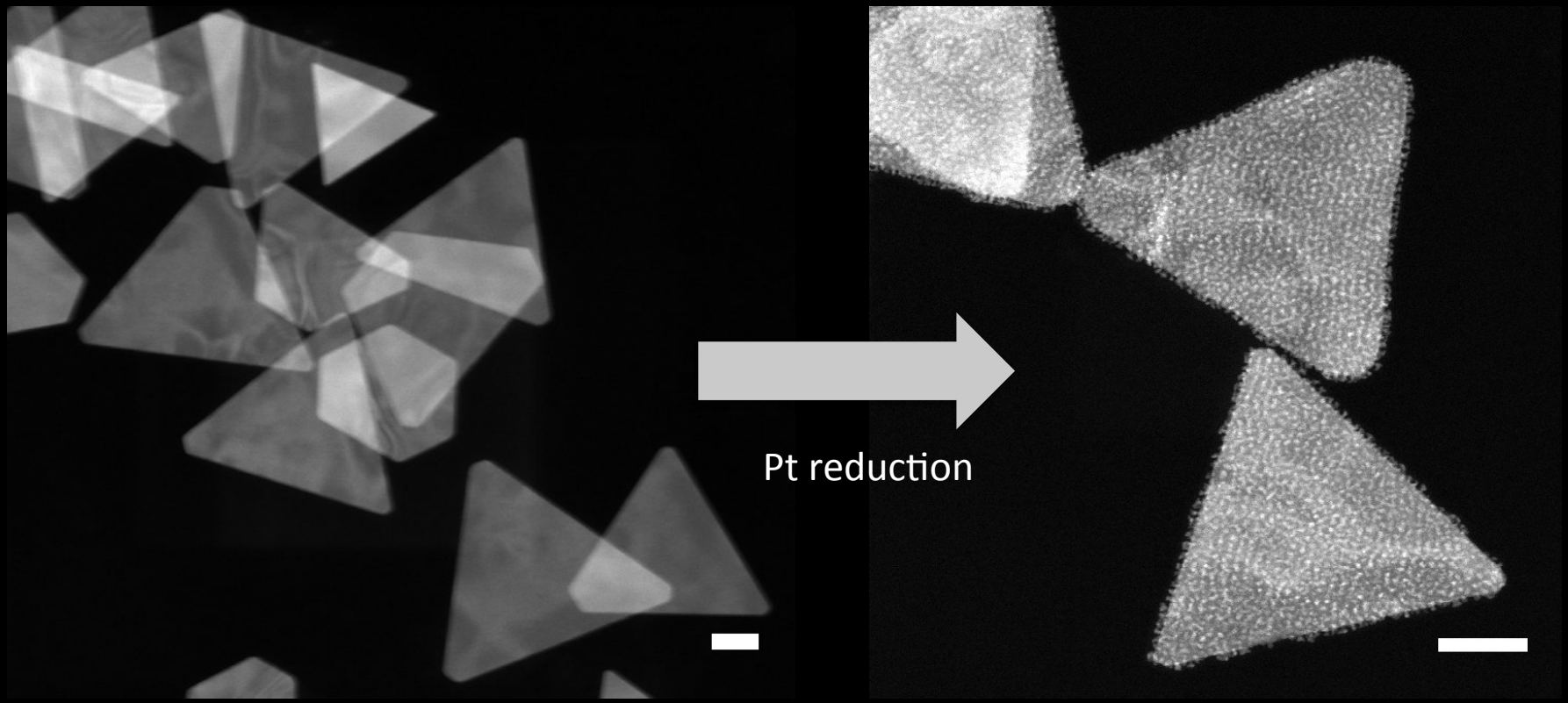
Pt



Au

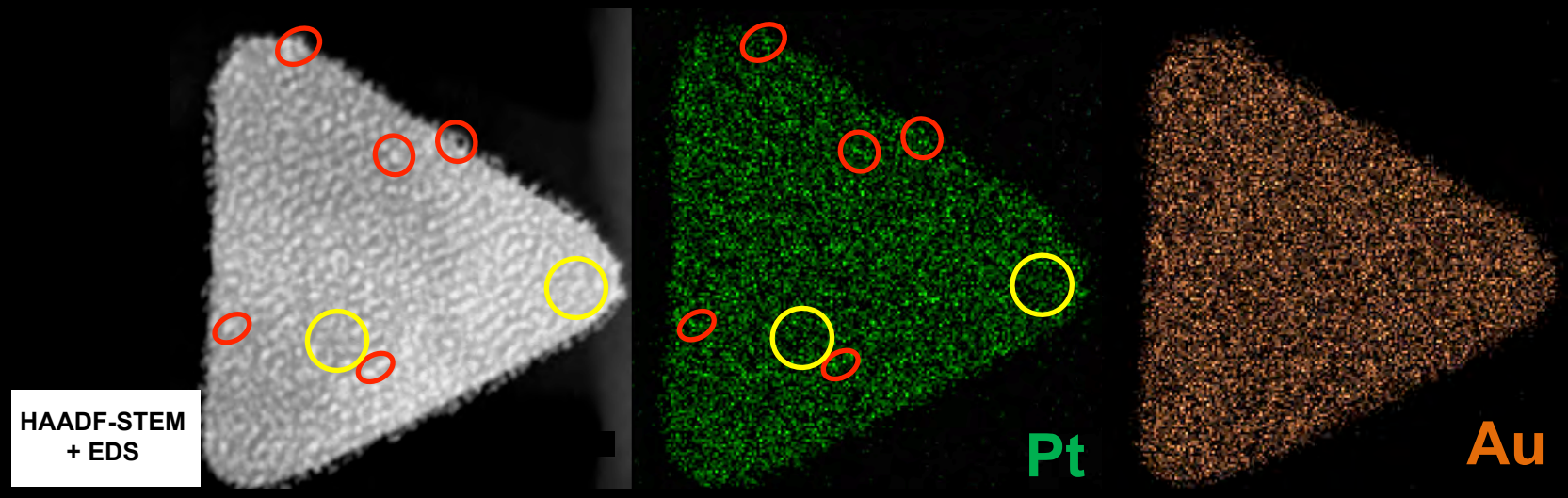


Pt-decorated Au platelets



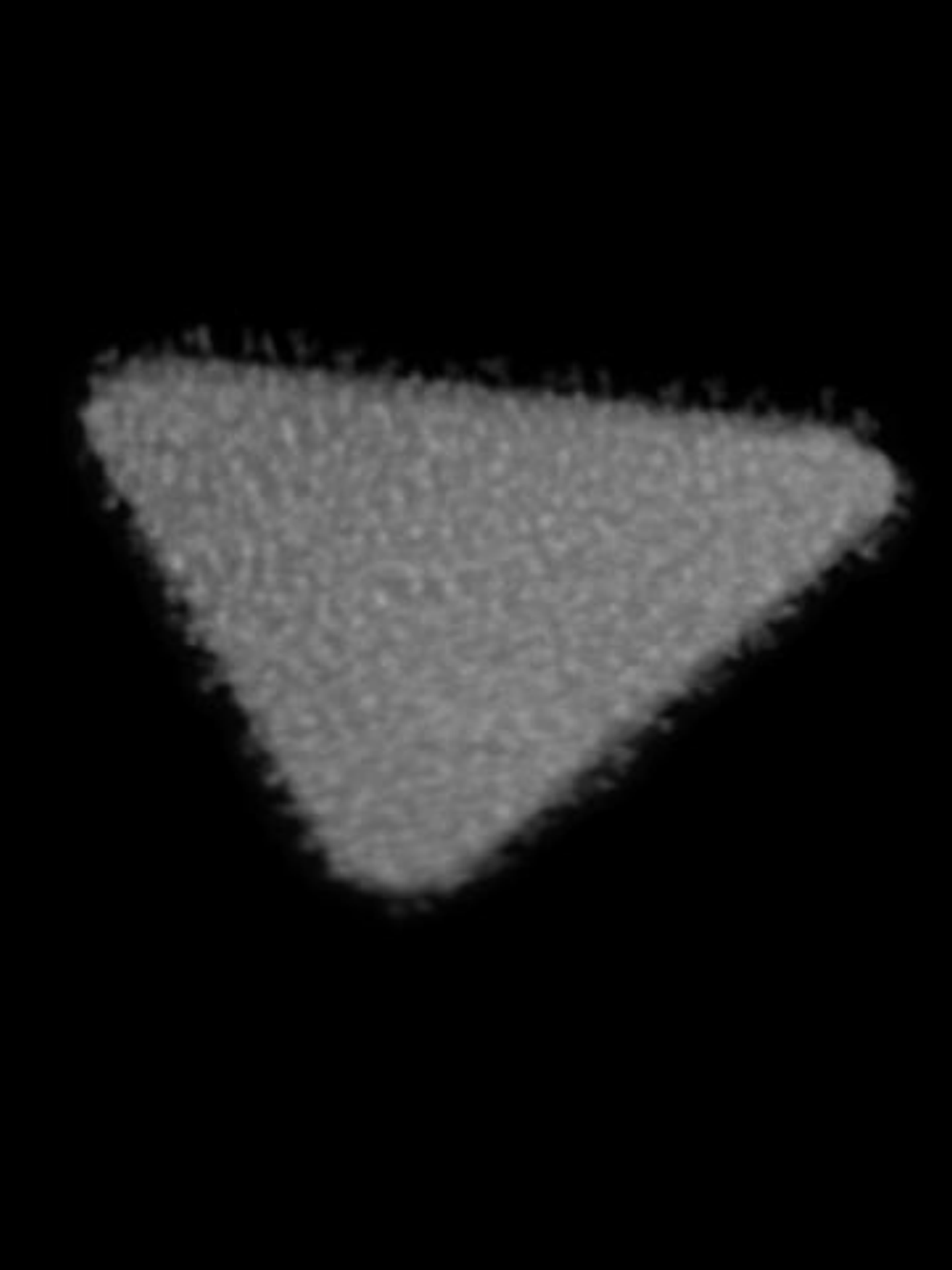
NB: For this & all following slides, all scalebars are 50 nm

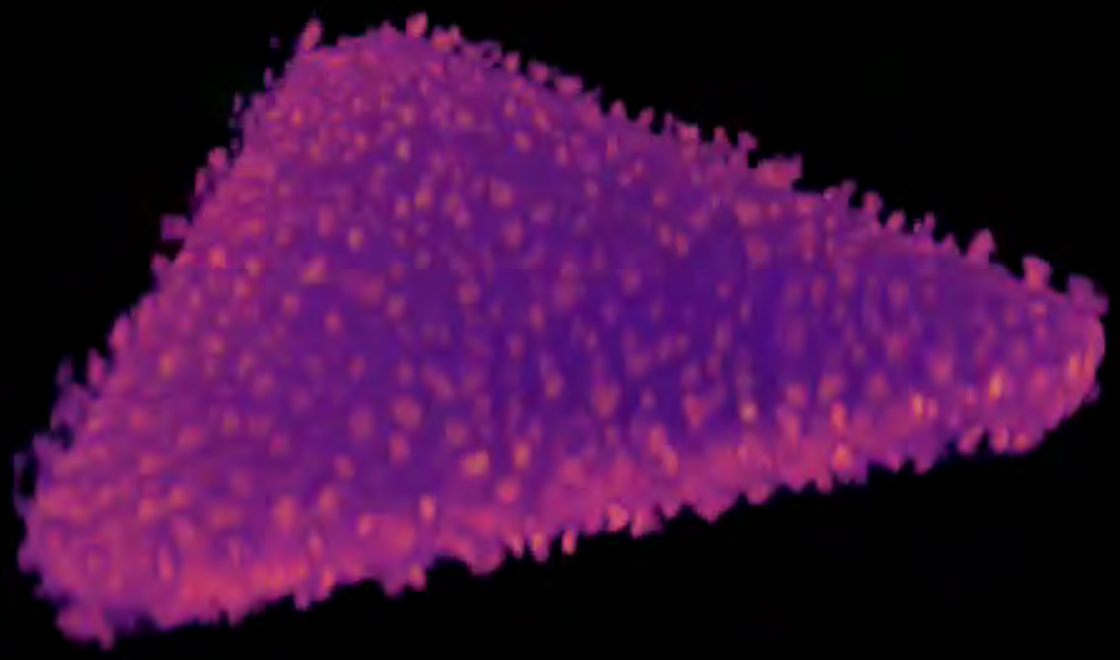
P. J. Straney, L. E. Marbella, C. M. Andolina, N. T. Nuhfer, J. E. Millstone, JACS (2014) 136, 7873



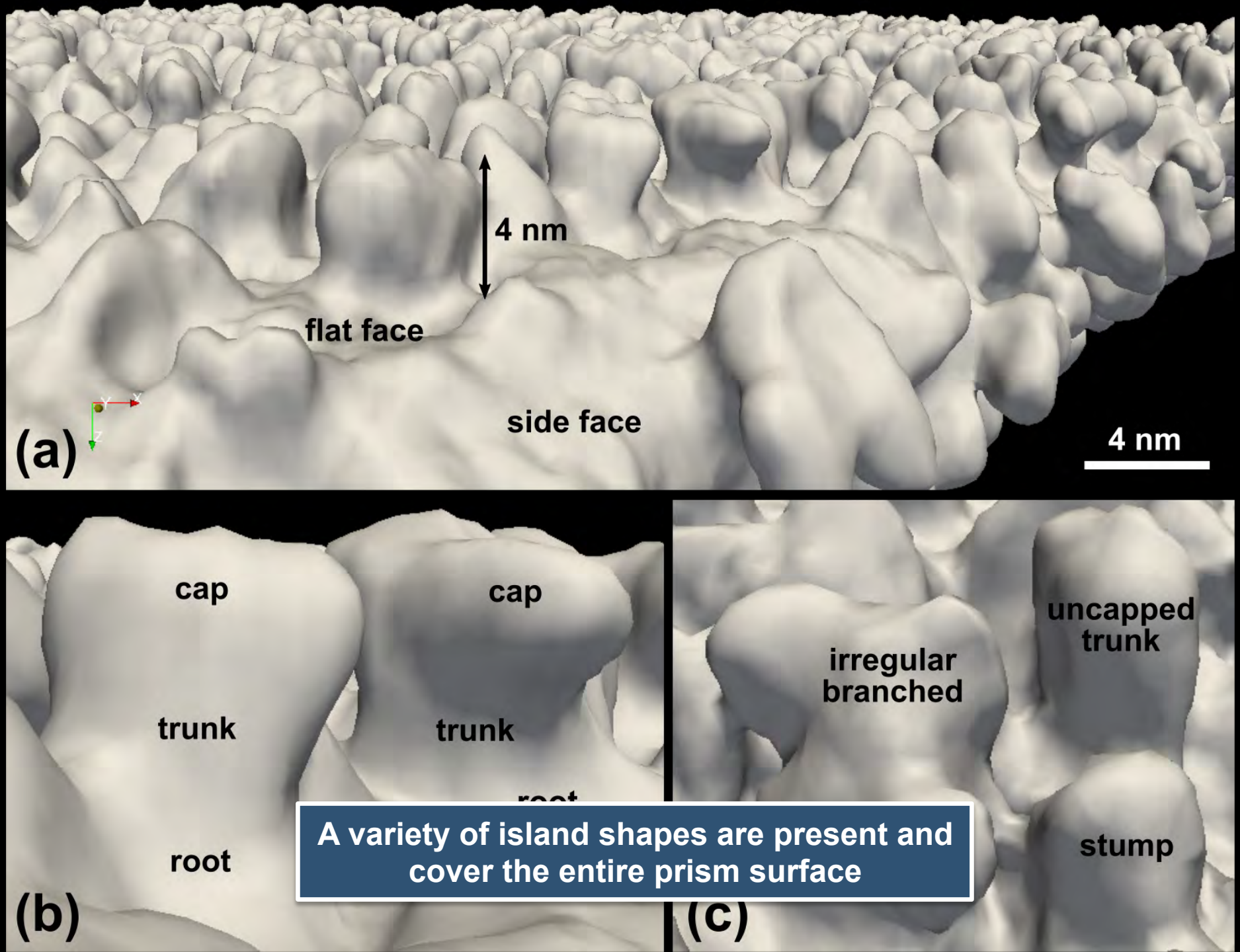
NPs are Au/Pt prisms

R. K. Leary, A. Kumar, P. Straney, S. Yazdi, P. A. Midgley, R. Dunin-Borkowski, J. E. Millstone, E. Ringe, J. Phys. Chem. C ASAP

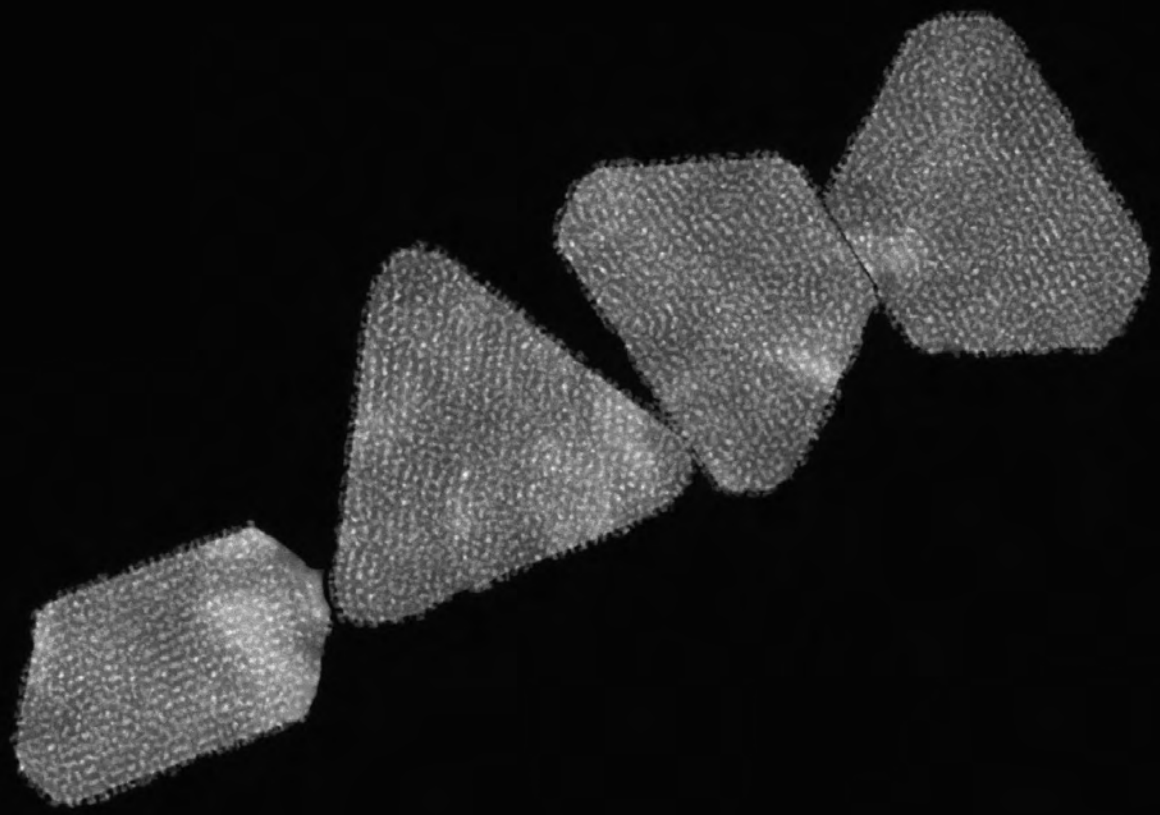




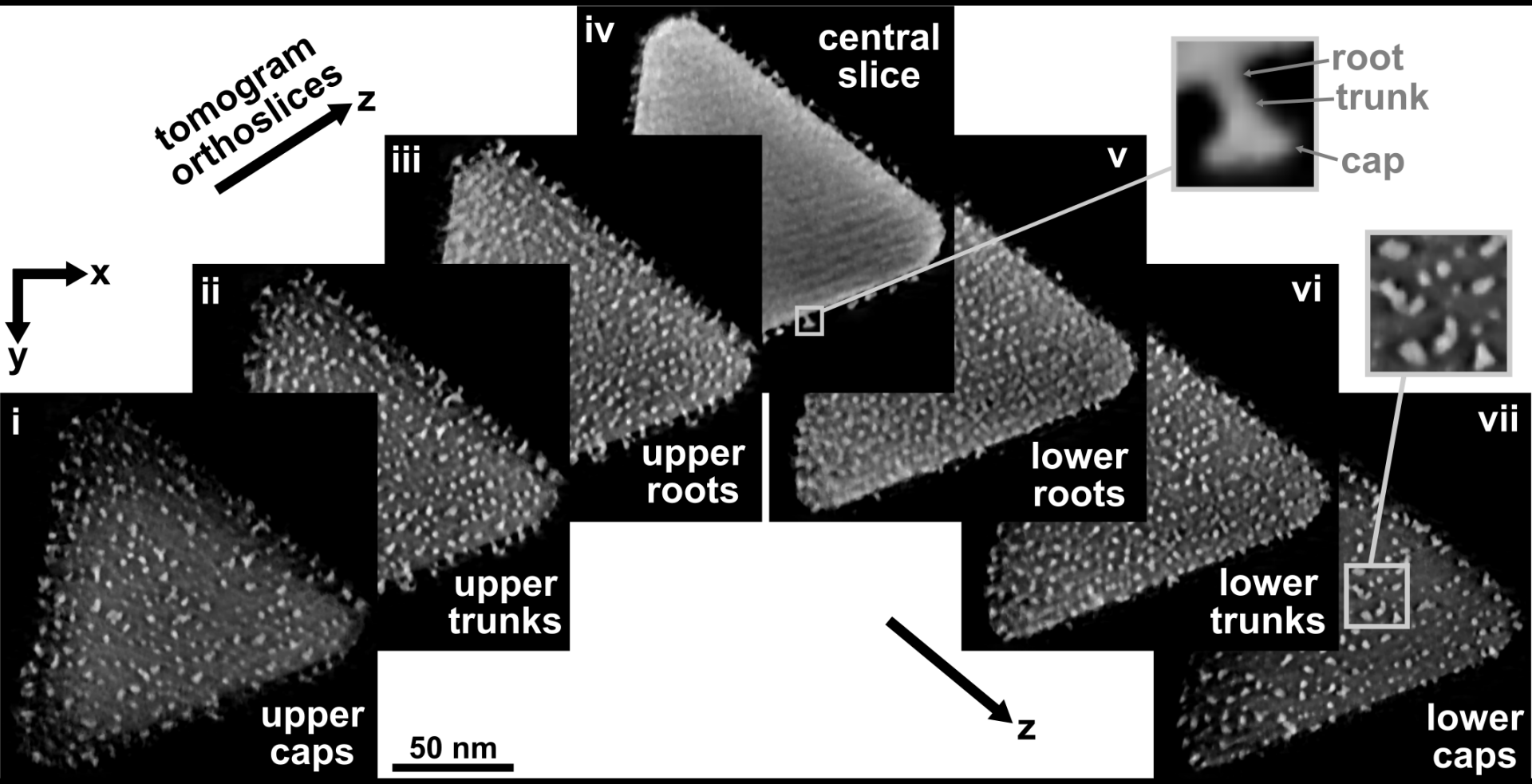
Islands are formed on sides AND flat surfaces

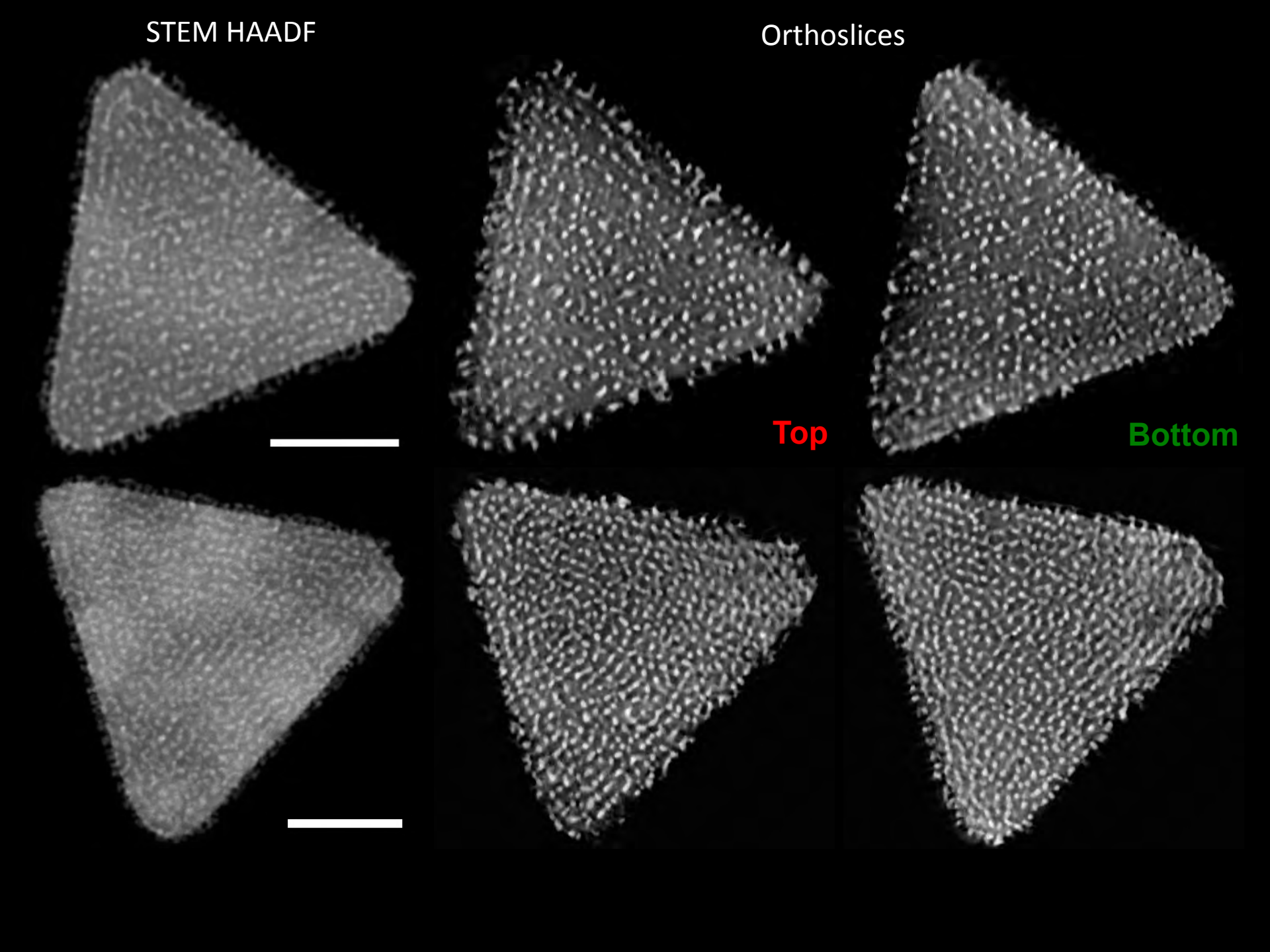


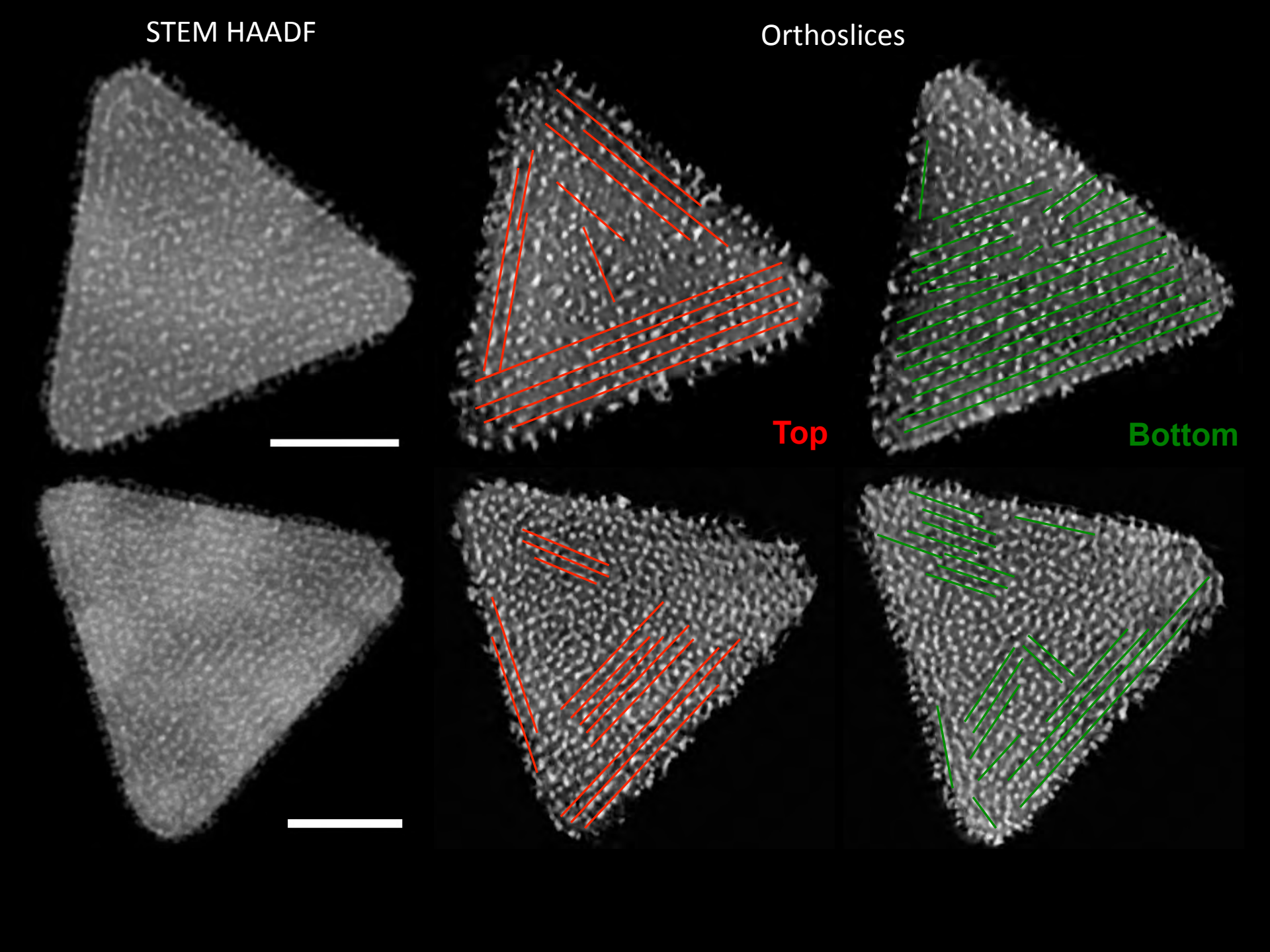
A variety of island shapes are present and cover the entire prism surface

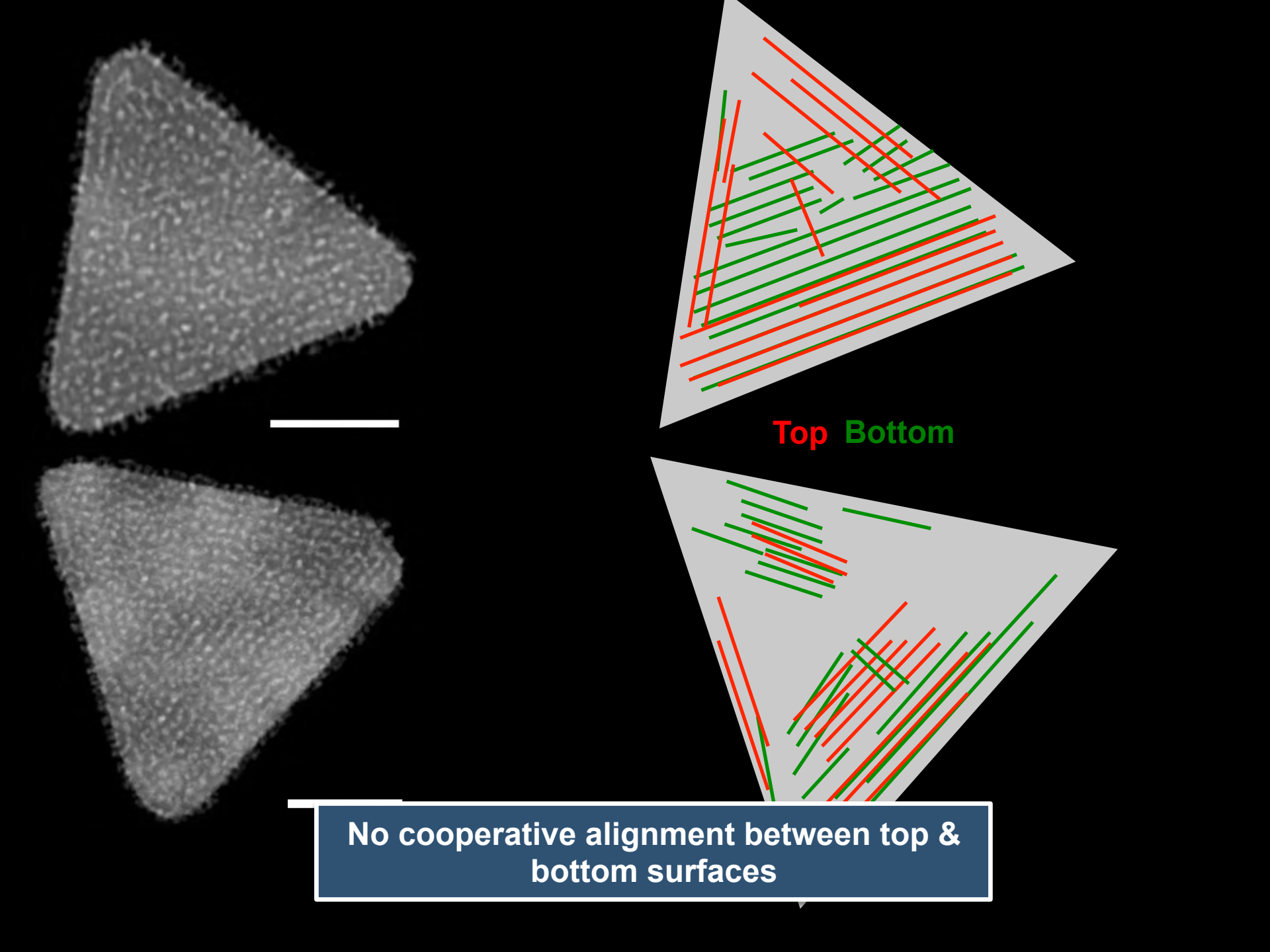


Islands appear to be aligned BUT STEM 2D projection does not differentiate btw top and bottom

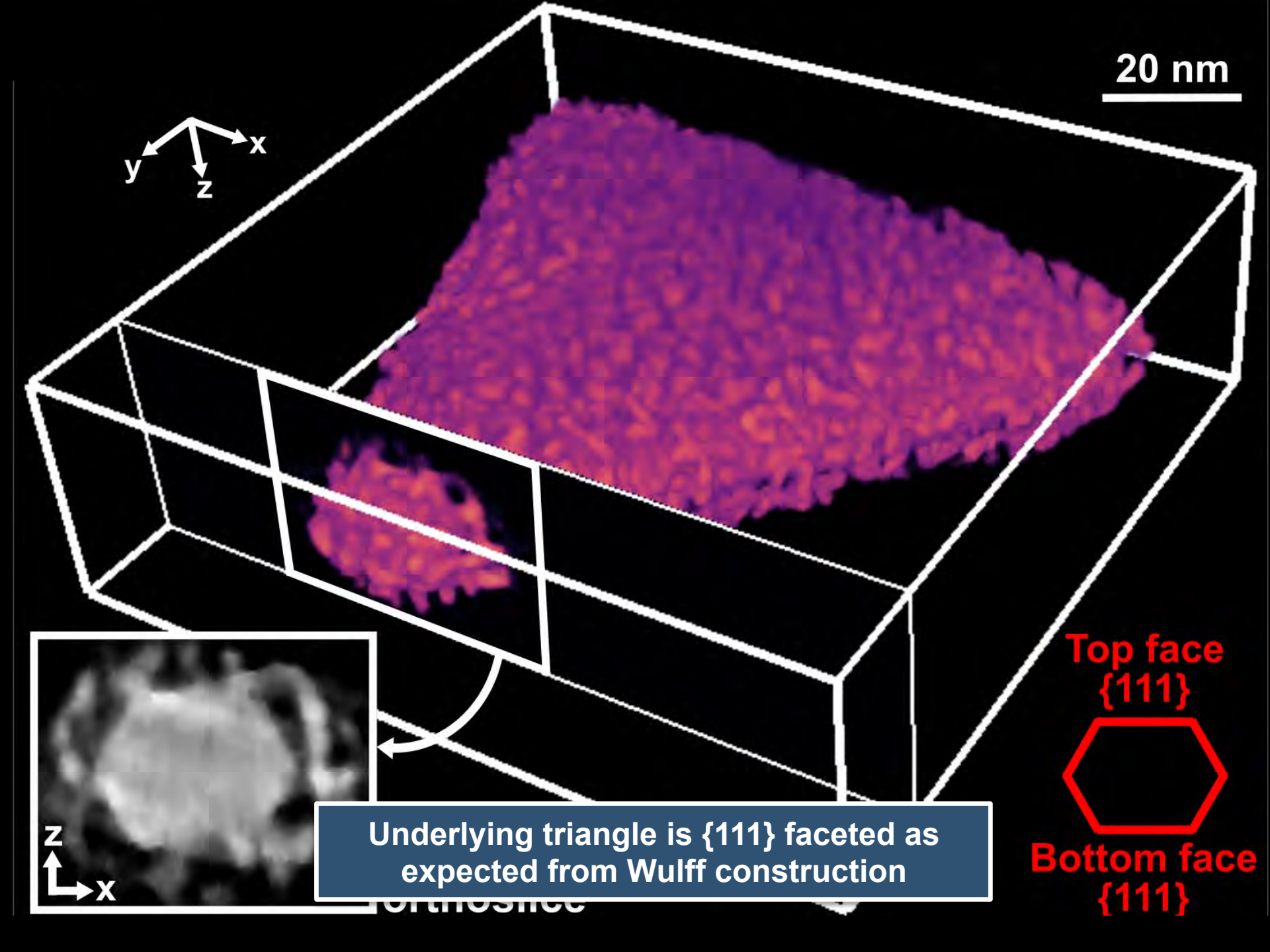

tomogram orthoslices
z
x
y
i
ii
iii
iv
v
vi
vii
central slice
root
trunk
cap
upper roots
lower roots
upper trunks
lower trunks
upper caps
lower caps
50 nm
z


STEM HAADF
Orthoslices
Top
Bottom


STEM HAADF
Orthoslices
Top
Bottom

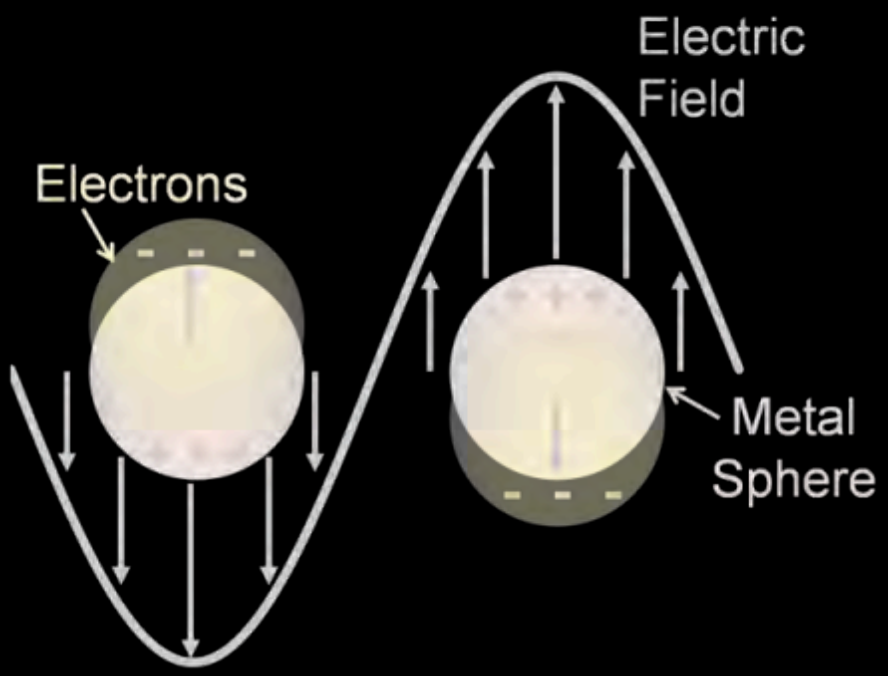


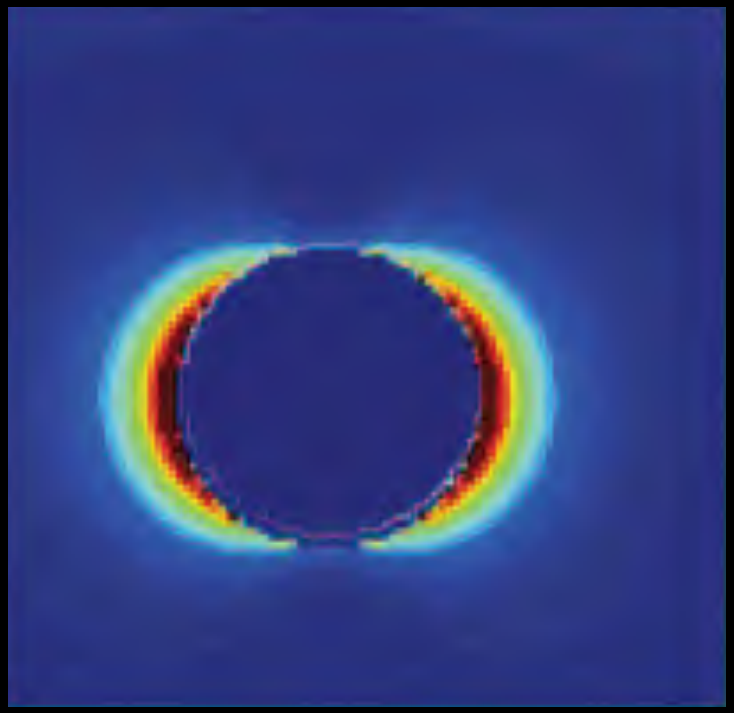
No cooperative alignment between top & bottom surfaces



Underlying triangle is {111} faceted as expected from Wulff construction

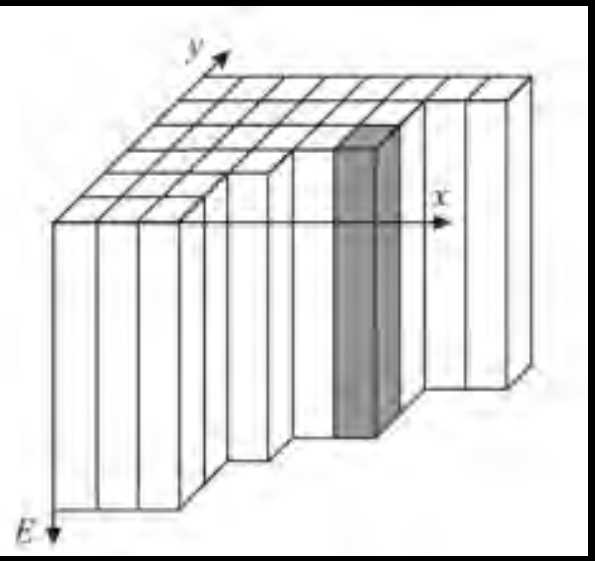
Localized Surface Plasmon Resonance (LSPR)





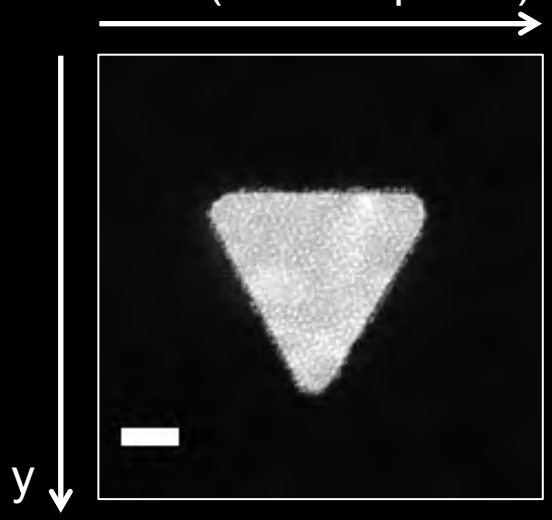
A. J. Haes, C. L. Haynes, A. D. McFarland, S. Zou, G. C. Schatz, R. P. Van Duyne, MRS Bull. (2005) 30, 368

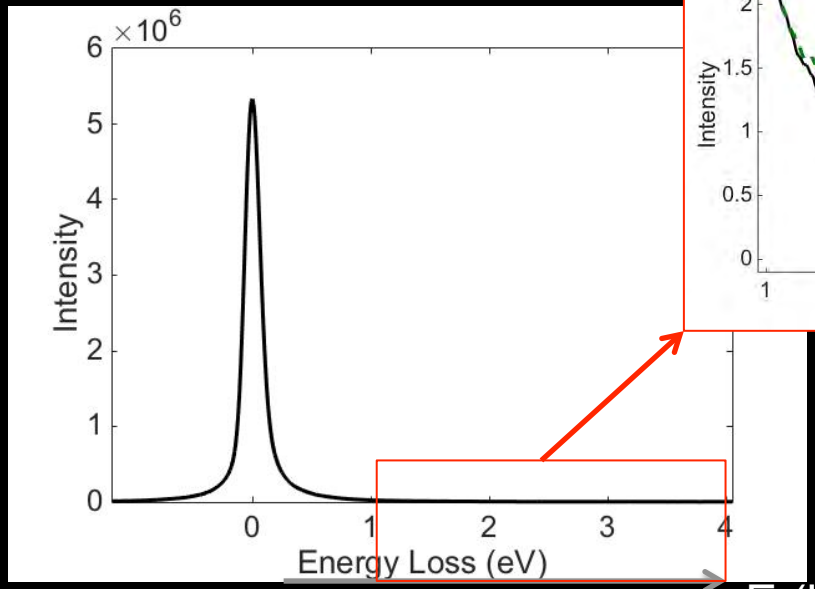
What Do the Modes Look Like?
EELS Provides Near-Field Information

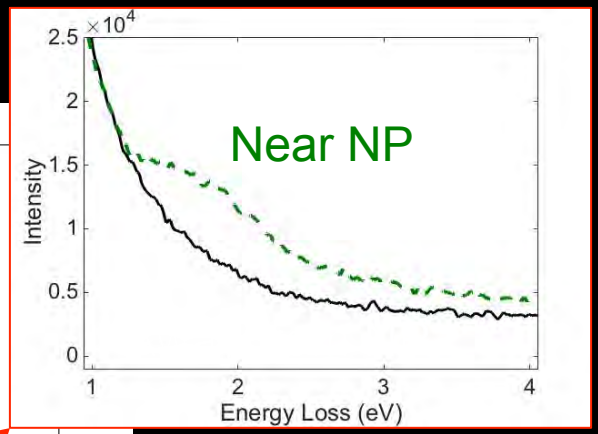


Scanning transmission electron microscopy
Electron-energy loss spectroscopy
(STEM-EELS)

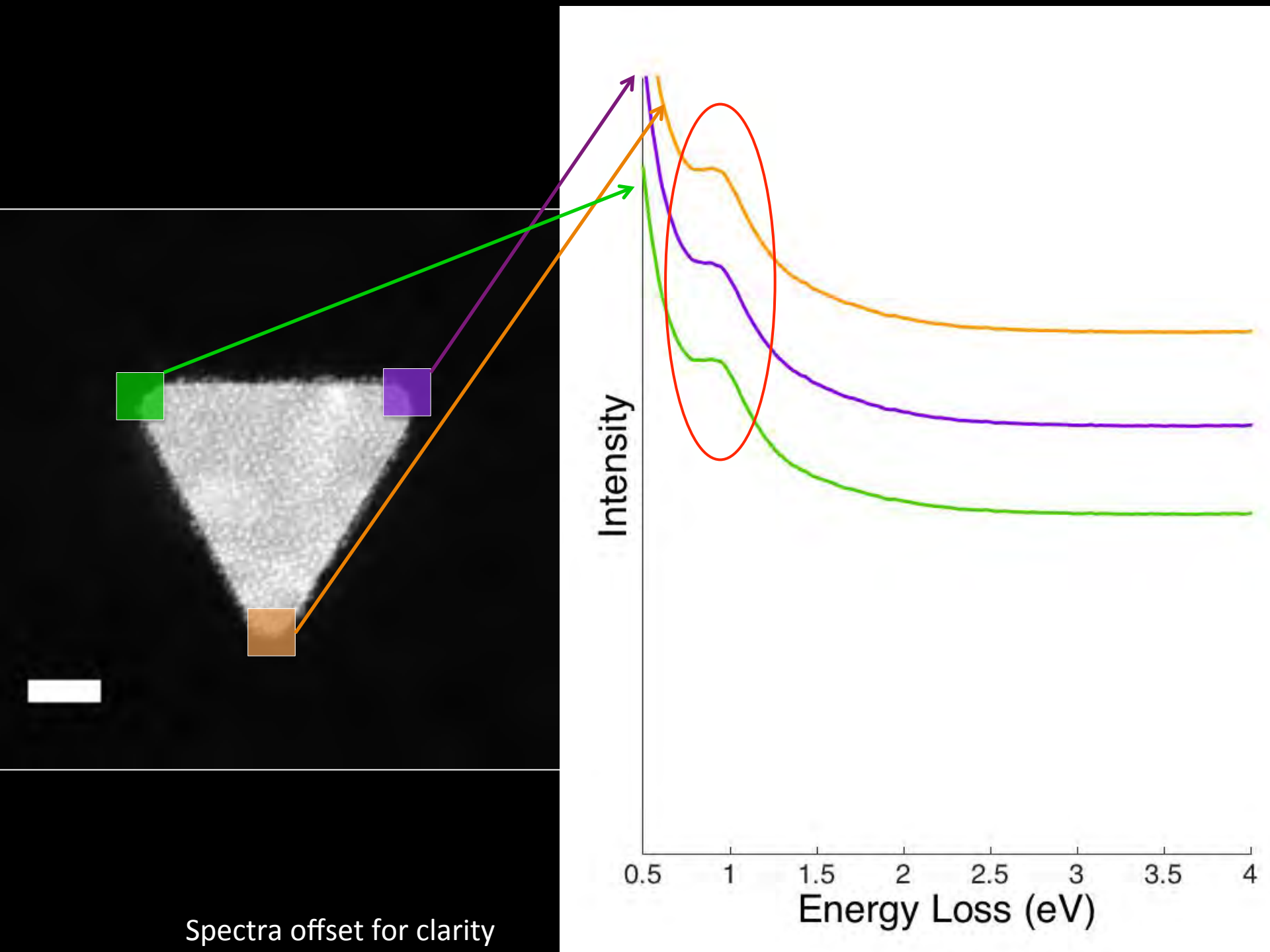
- Electron acts as a unpolarized white light
- Can excite all plasmons
- Bright & dark modes
- Local maps
- Monochromator needed for low energies

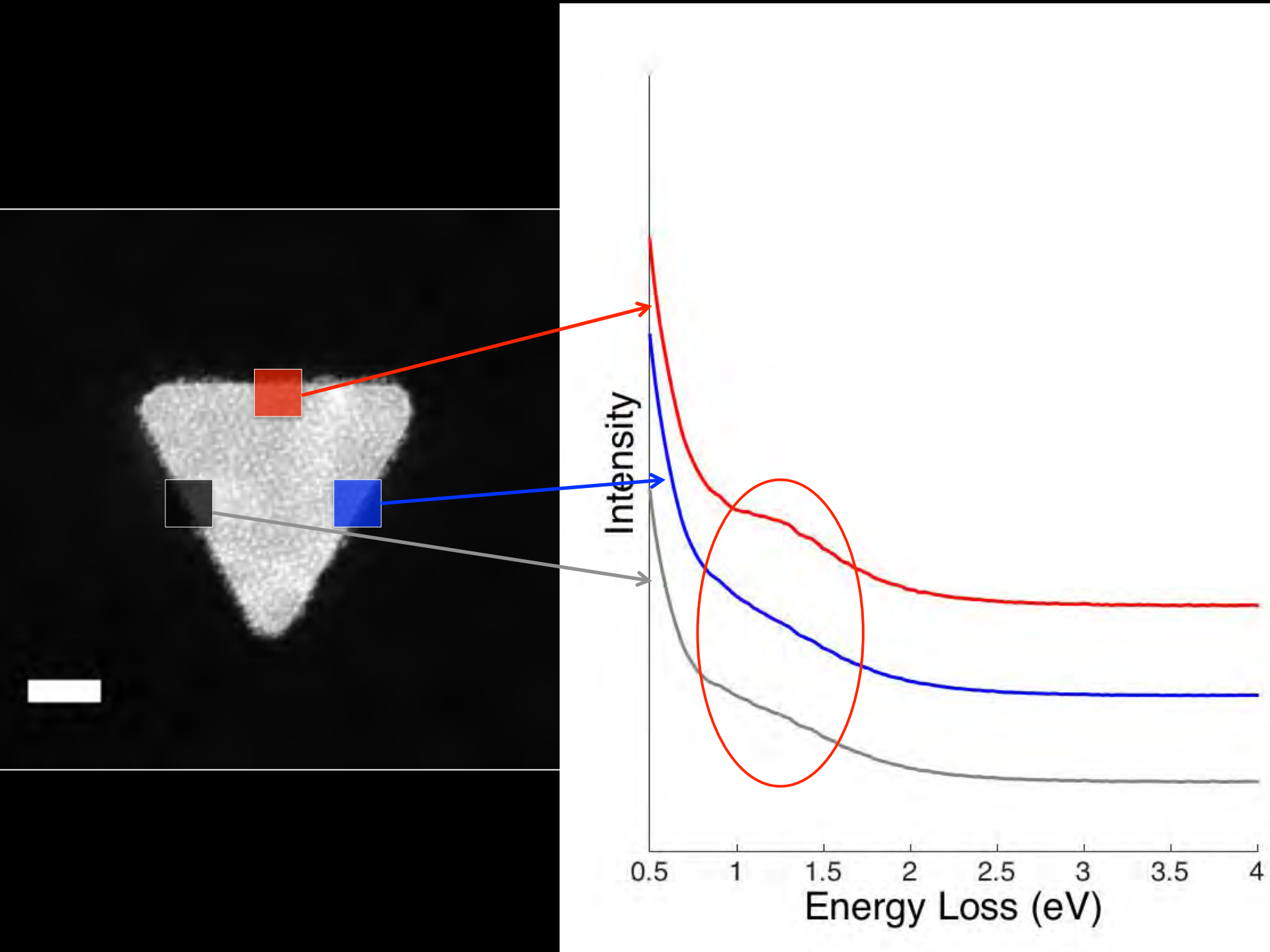


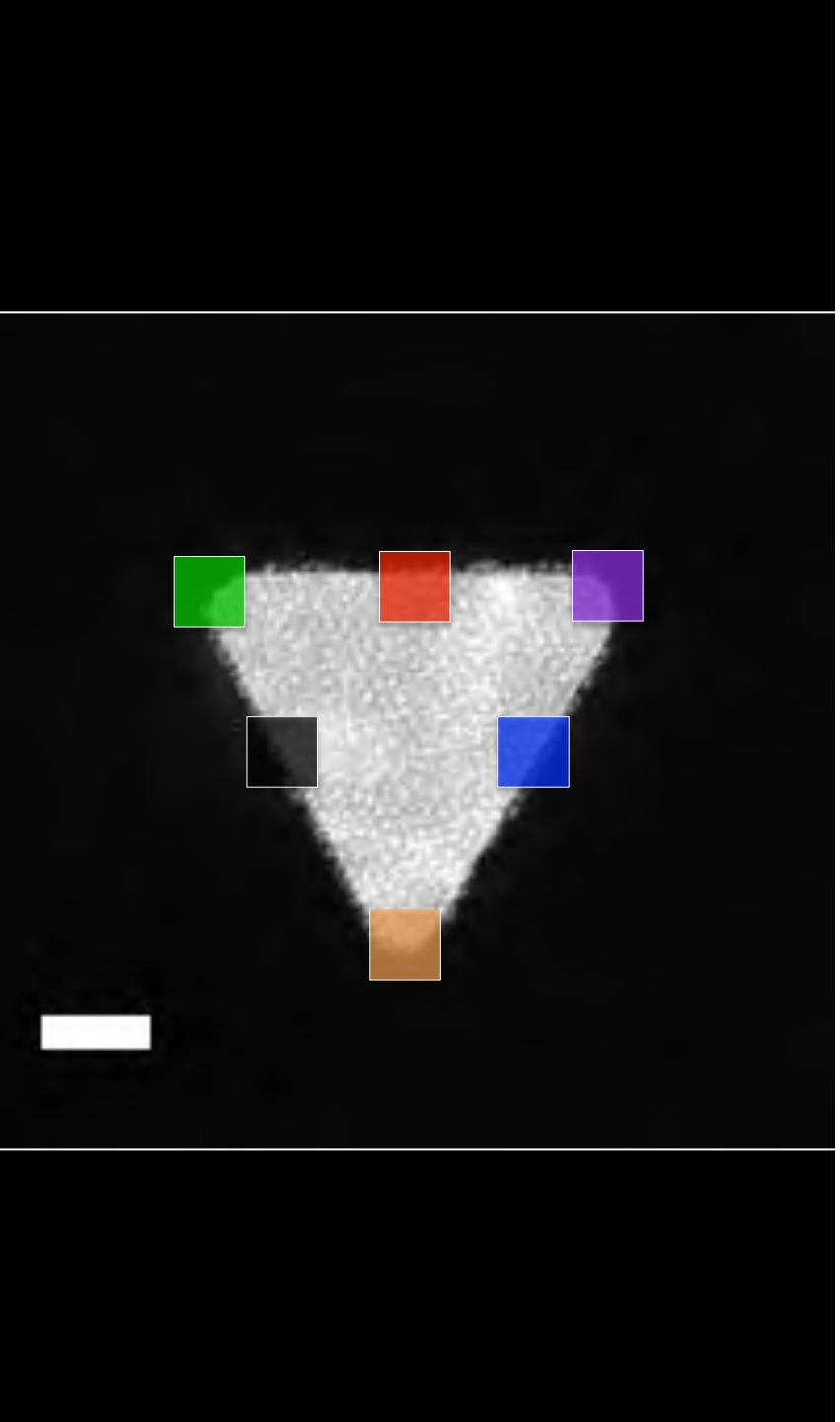


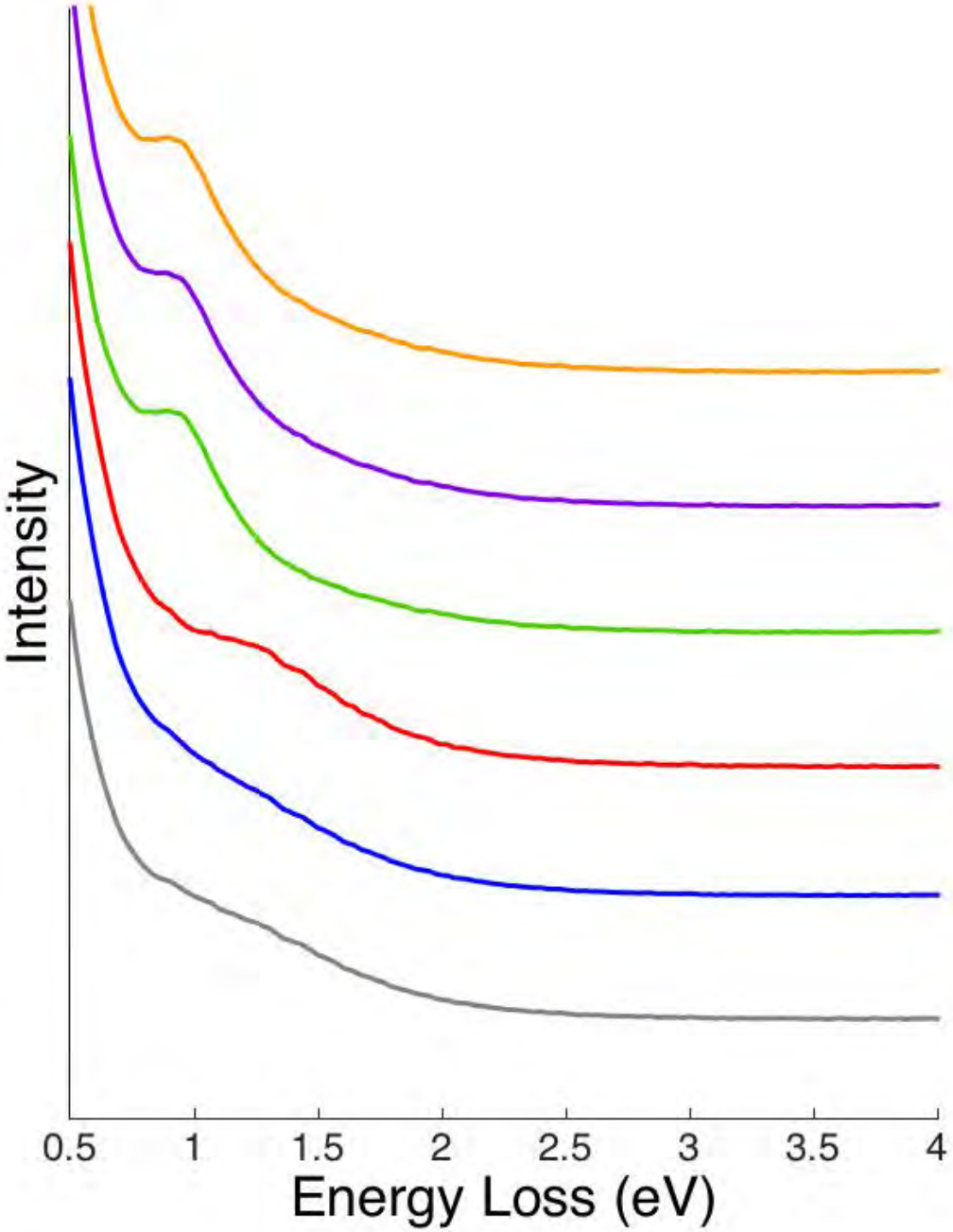


E (low loss region)

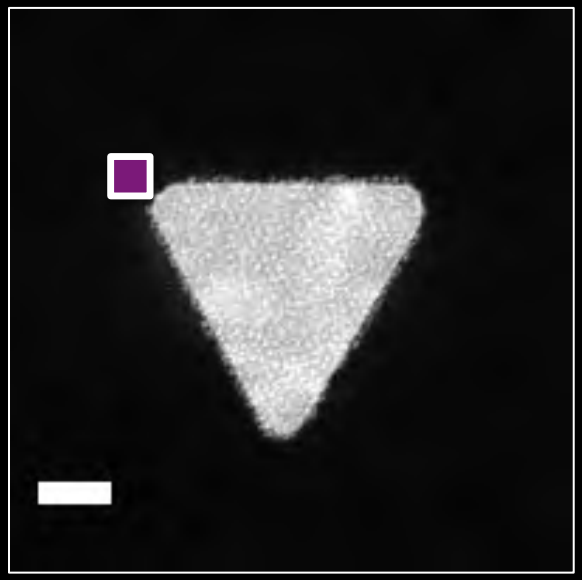

Intensity
0.5
1
1.5
2
2.5
3
3.5
4
Energy Loss (eV)
Spectra offset for clarity

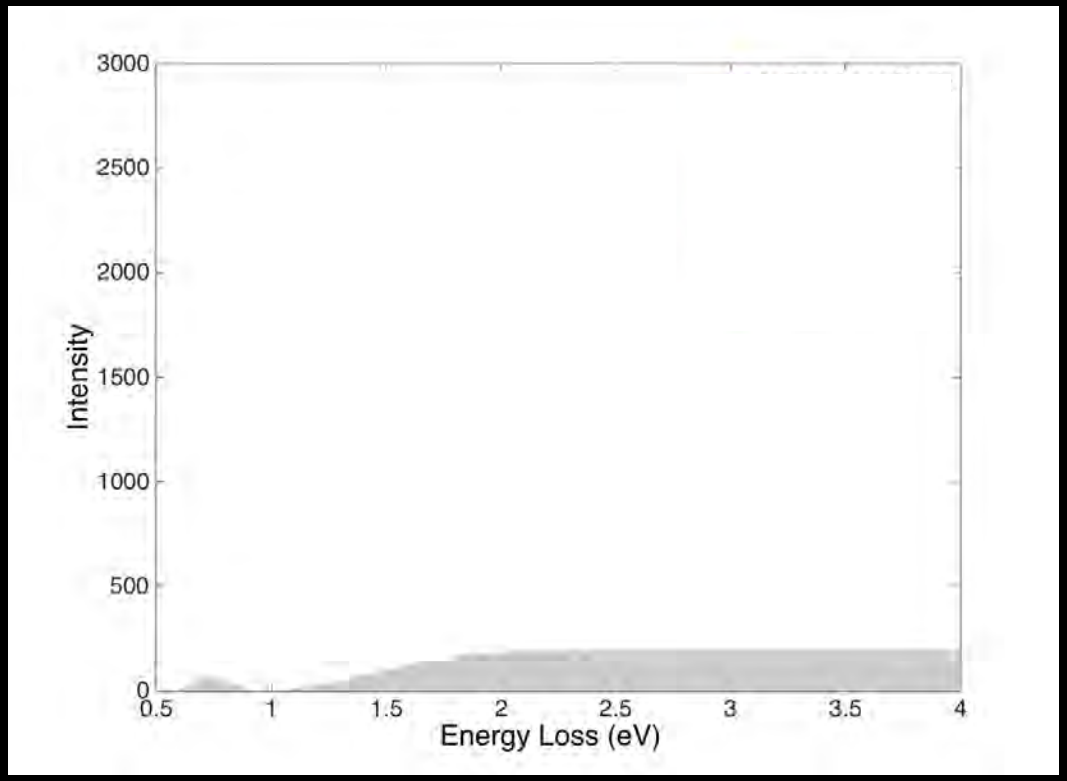

Intensity
0.5
1
1.5
2
2.5
3
3.5
4
Energy Loss (eV)

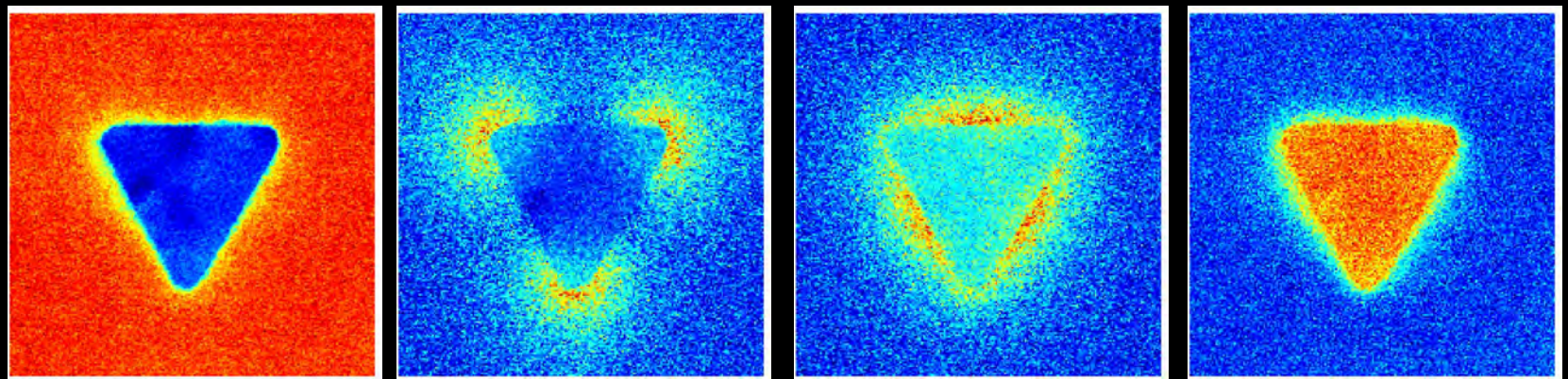



Intensity
0.5
1
1.5
2
2.5
3
3.5
4
Energy Loss (eV)

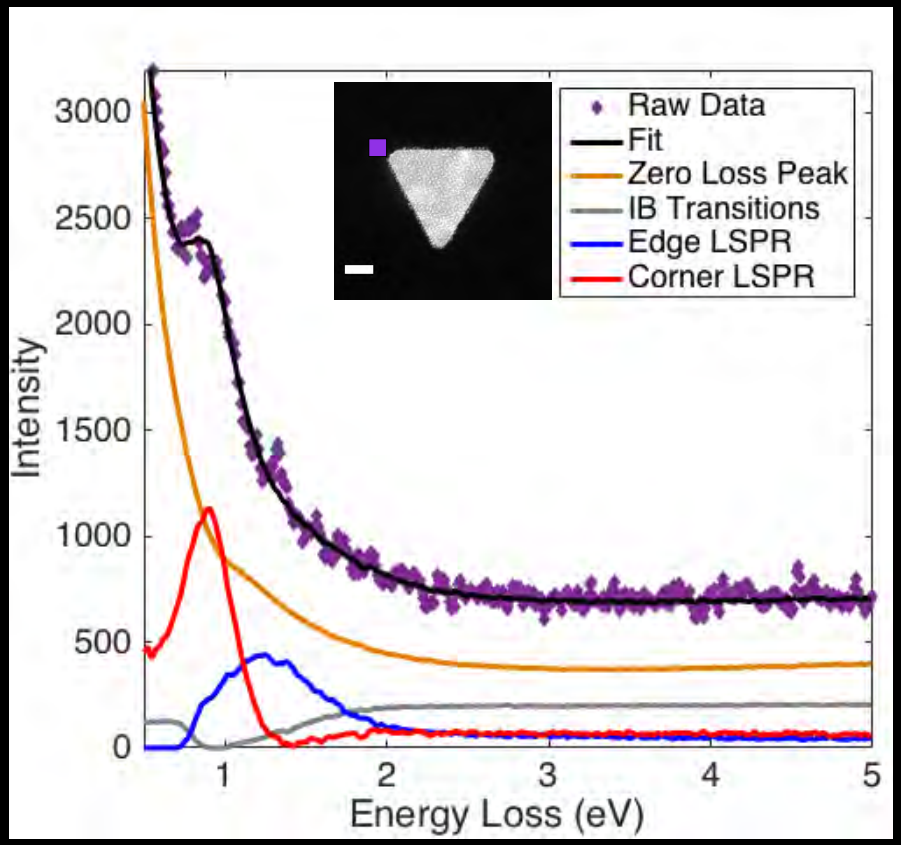
Extracting Plasmon Modes with Non-Negative Matrix Factorization (NMF)

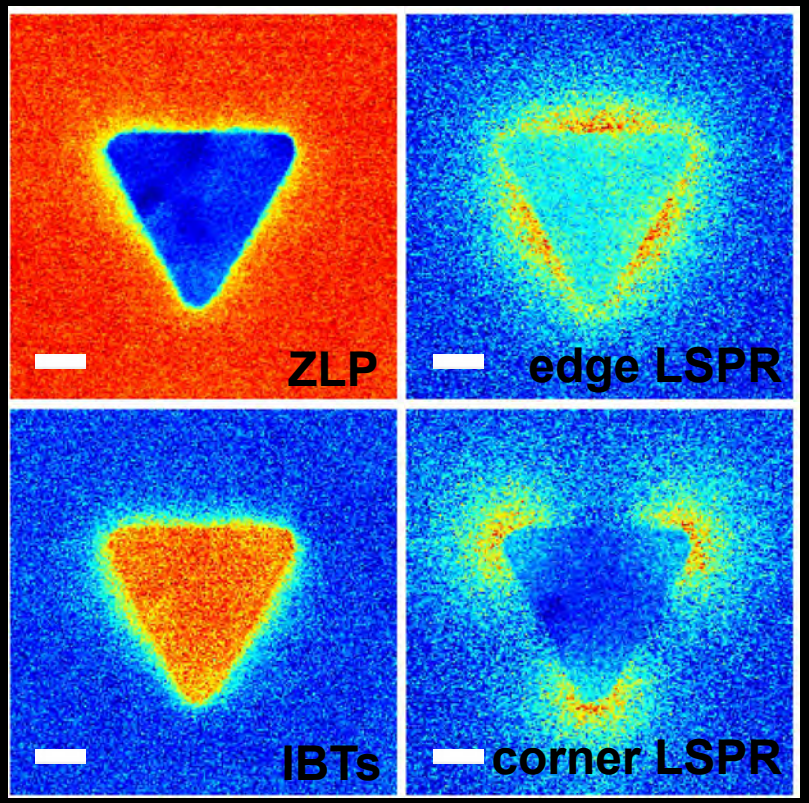




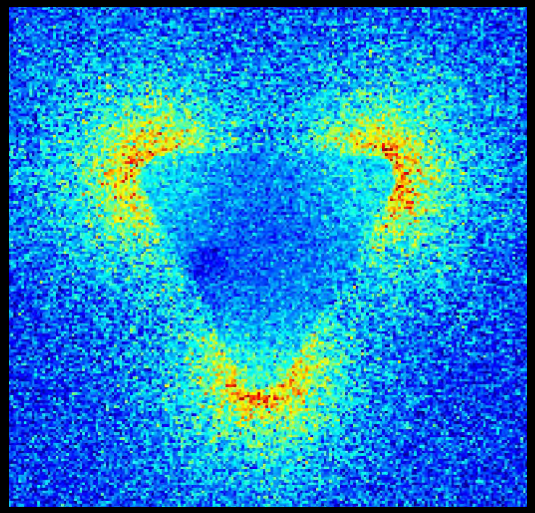


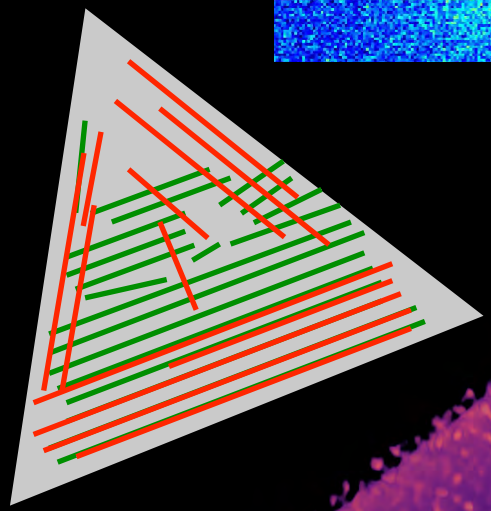
Extracting Plasmon Modes with Non-Negative Matrix Factorization (NMF)

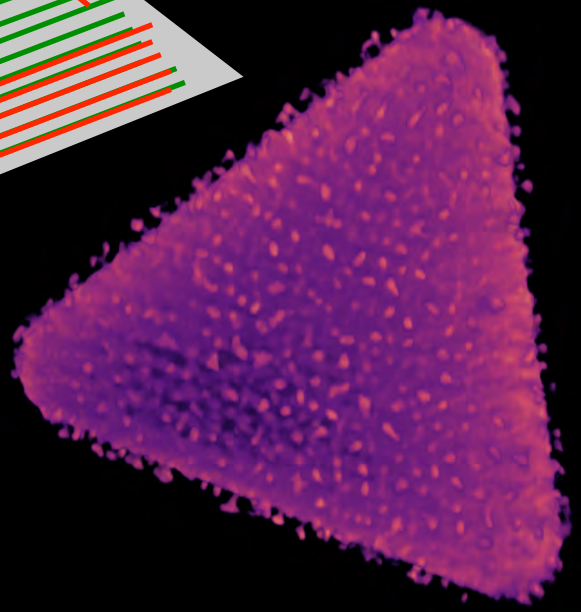




Au/Pt nanoprisms sustain localized plasmon resonances despite the presence of Pt, a lossy plasmonic metal







NPs are Au/Pt prisms

Islands are formed on sides AND flat surfaces

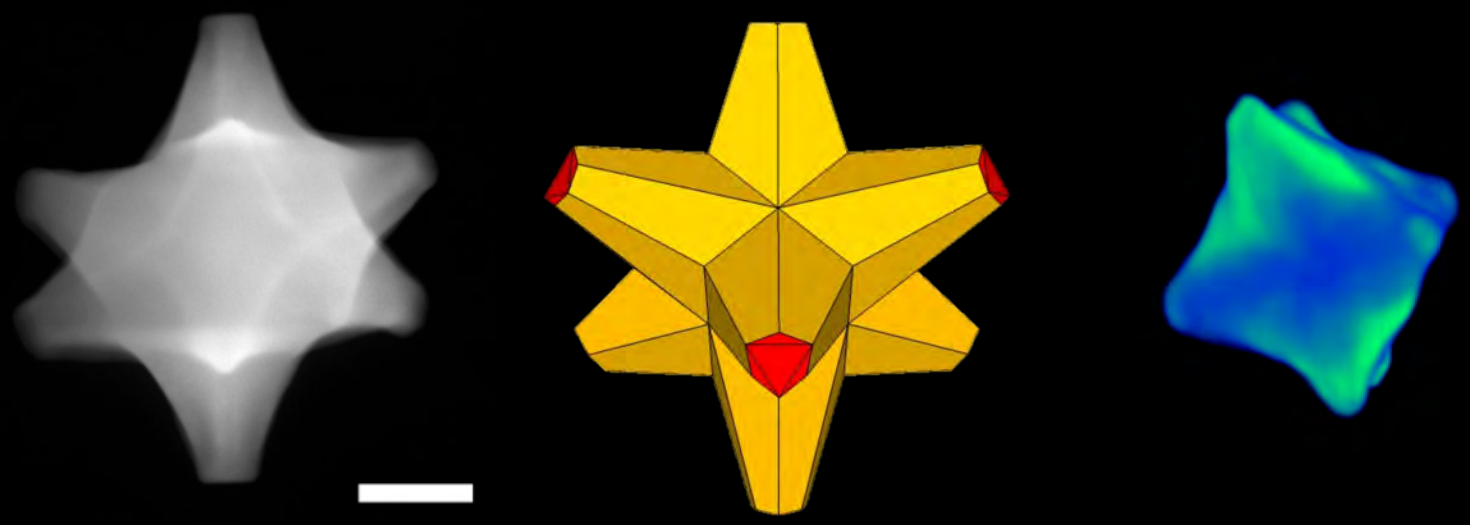
No cooperative alignment between top & bottom surfaces

Underlying triangle is {111} faceted as expected from Wulff construction

Au/Pt nanoprisms sustain localized plasmon resonances despite the presence of Pt, a poor plasmonic metal

R. K. Leary, A. Kumar, P. Straney, S. Yazdi, P. A. Midgley, R. Dunin-Borkowski, J. E. Millstone, E. Ringe, J. Phys. Chem. C ASAP

Octopods

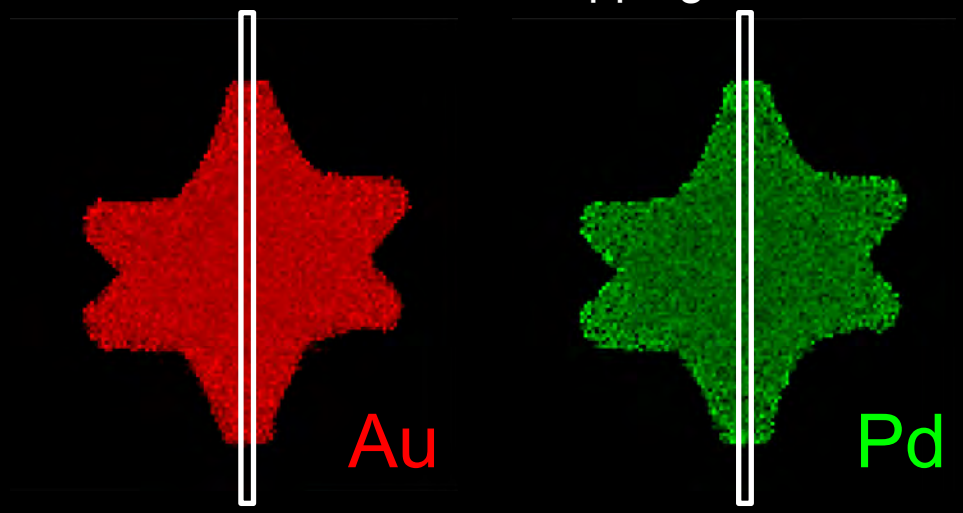


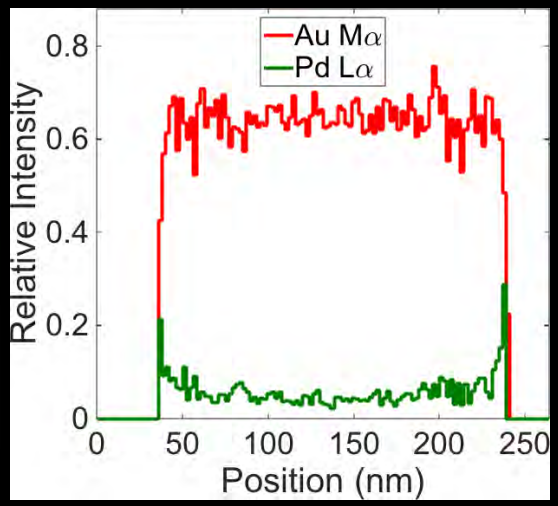
8 branches along the <111> directions

E. Ringe, C. J. DeSantis, S. M. Collins, M. Duchamp, R. E. Dunin-Borkowski, S. E. Skrabalak, and P. A. Midgley, Sci. Rep. (2015), 5, 17431

8-Branched Au/Pd Octopods

STEM-EDS Mapping

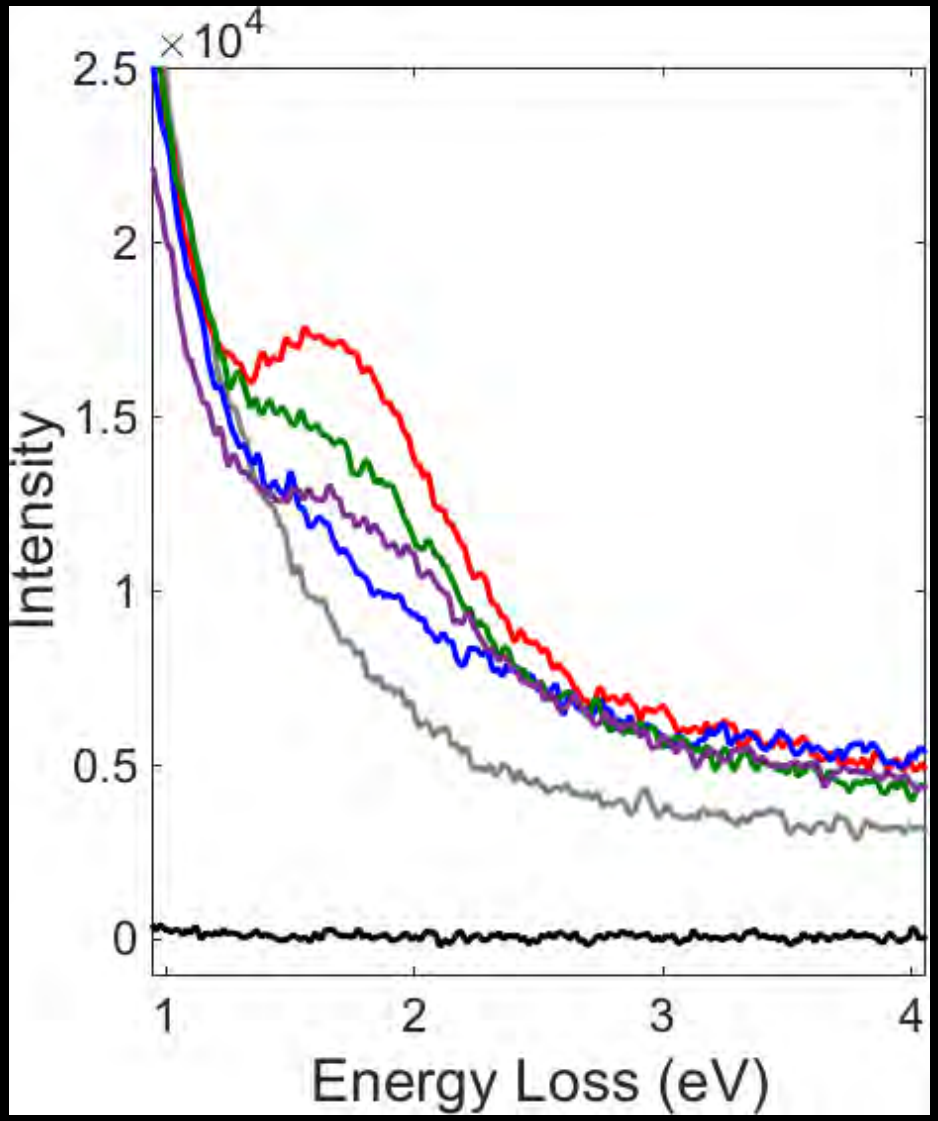


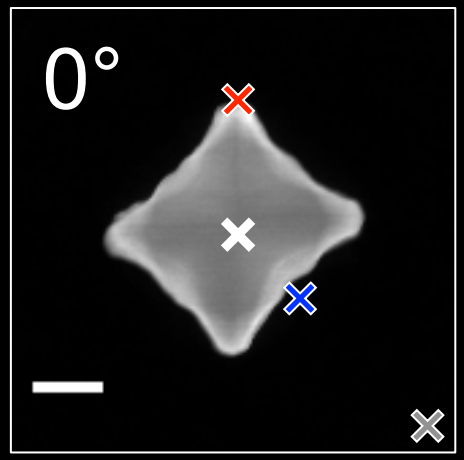


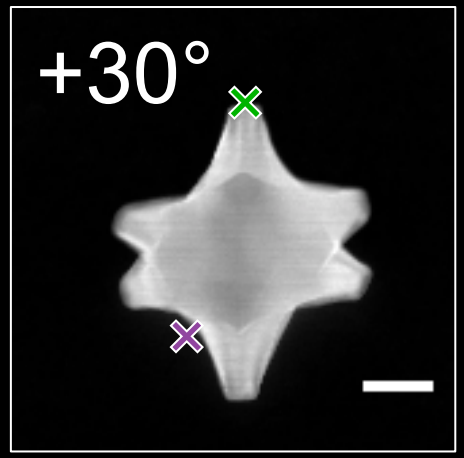
Pd mainly at the surface

E. Ringe, C. J. DeSantis, S. M. Collins, M. Duchamp, R. E. Dunin-Borkowski, S. E. Skrabalak, and P. A. Midgley, Sci. Rep. (2015), 5, 17431

Electron Energy Loss Spectroscopy

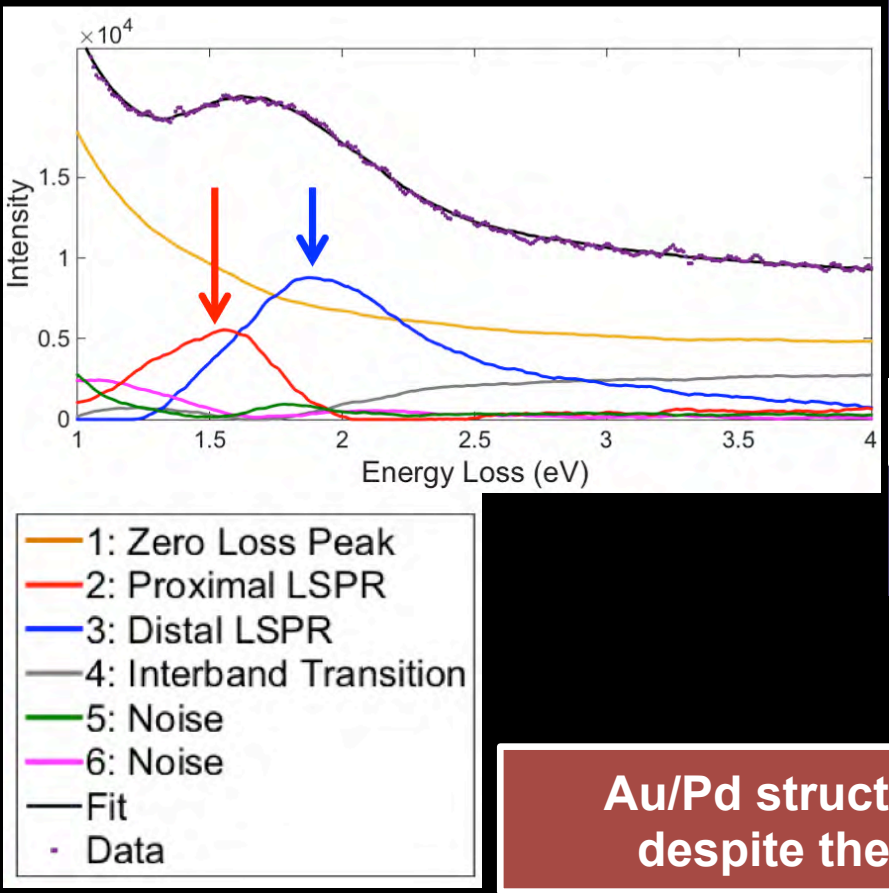


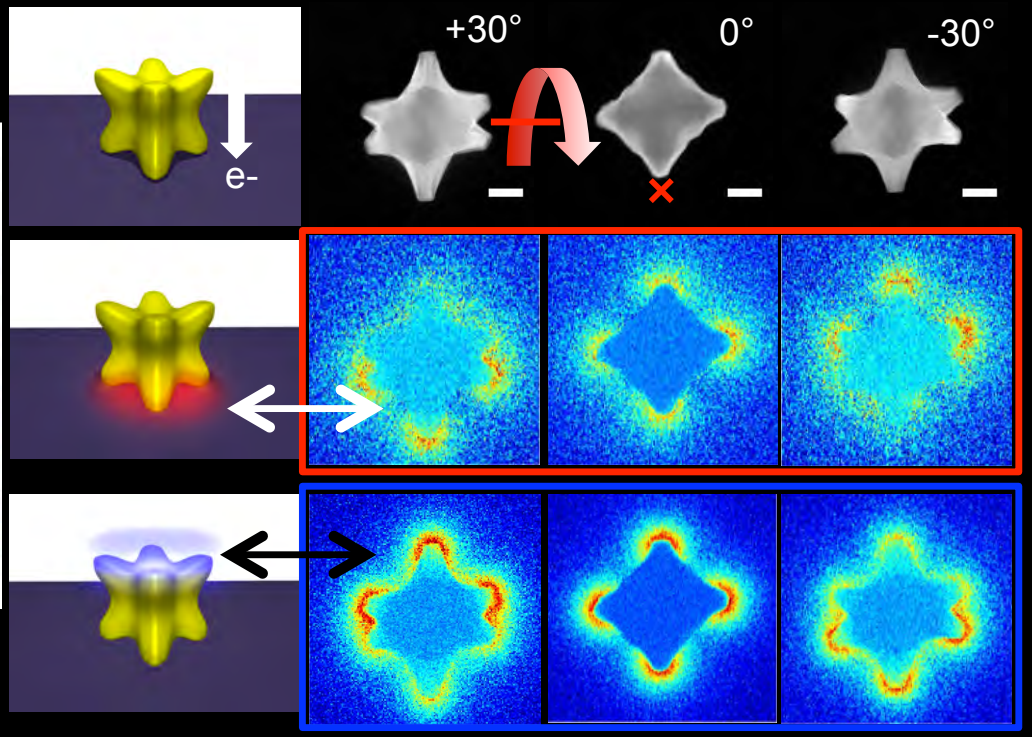




E. Ringe, C. J. DeSantis, S. M. Collins, M. Duchamp, R. E. Dunin-Borkowski, S. E. Skrabalak, and P. A. Midgley, Sci. Rep. (2015), 5, 17431

EELS Plasmon Mapping of Octopods

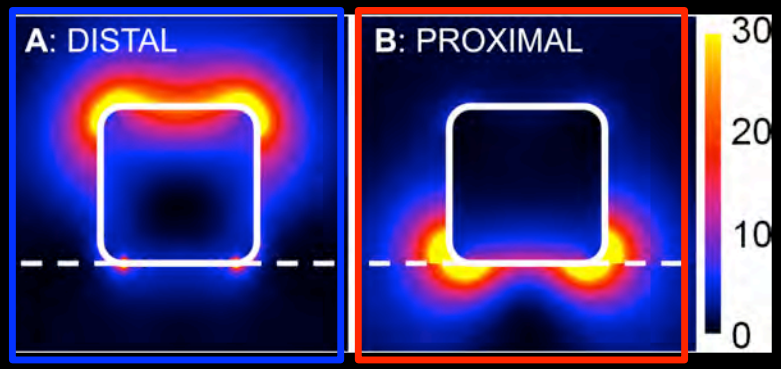




Au/Pd structures have strong LSPR despite the presence of lossy Pd

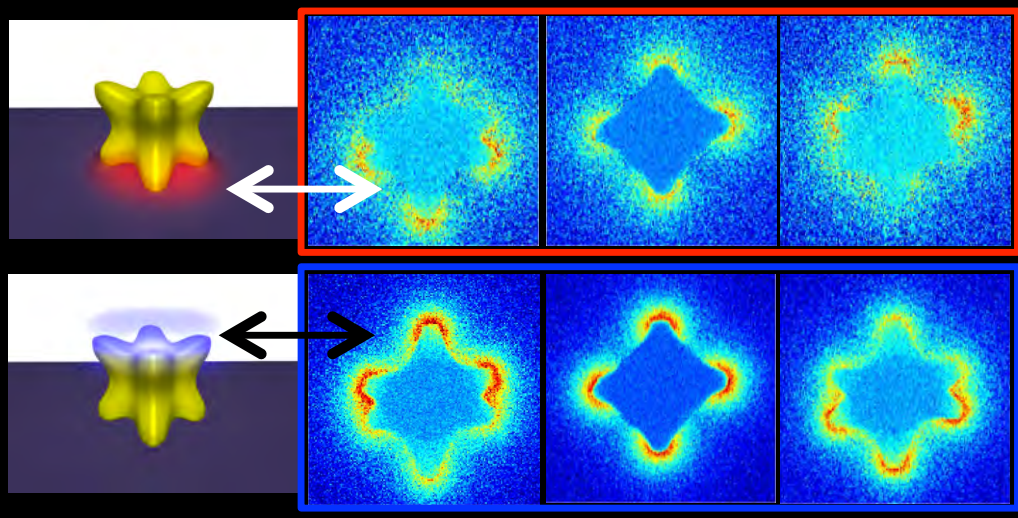
E. Ringe, C. J. DeSantis, S. M. Collins, M. Duchamp, S. E. Skrabalak, R. E. Dunin-Borkowski, and P. A. Midgley, Sci. Rep. (2015), 5, 17431

Ag Nanocubes



E. Ringe, J. M. McMahon, K. Sohn, C. Cobley, Y. Xia, J. Huang, G. C. Schatz, L. D. Marks, R. P. Van Duyne, J. Phys. Chem. C, (2010) 114, 12511

Au/Pd Octopods



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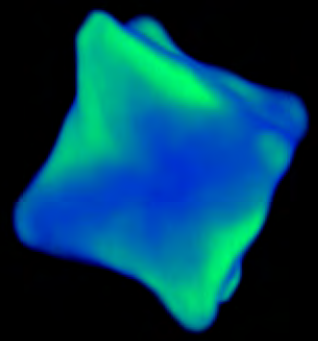
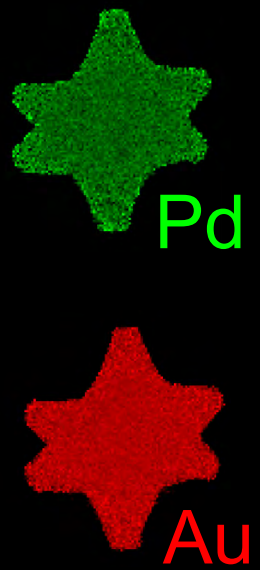
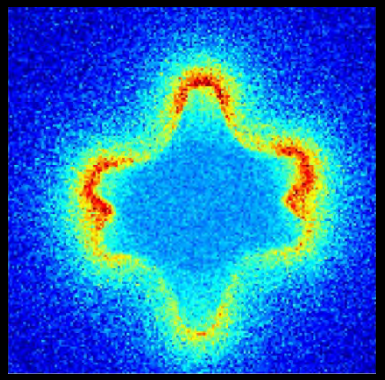
LSPR in Au/Pd octopods can couple with substrate through Pd-rich tips







8 branches along the <111> directions

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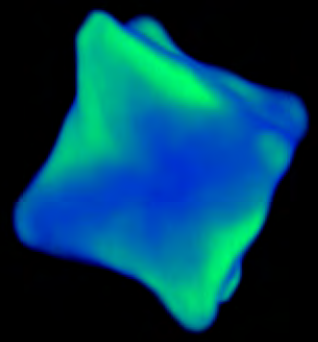
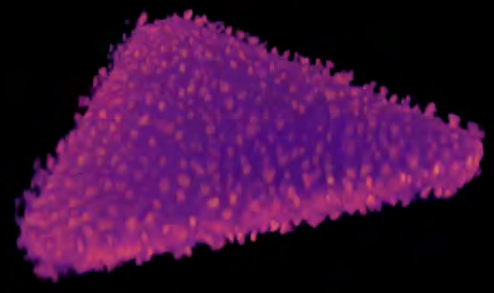
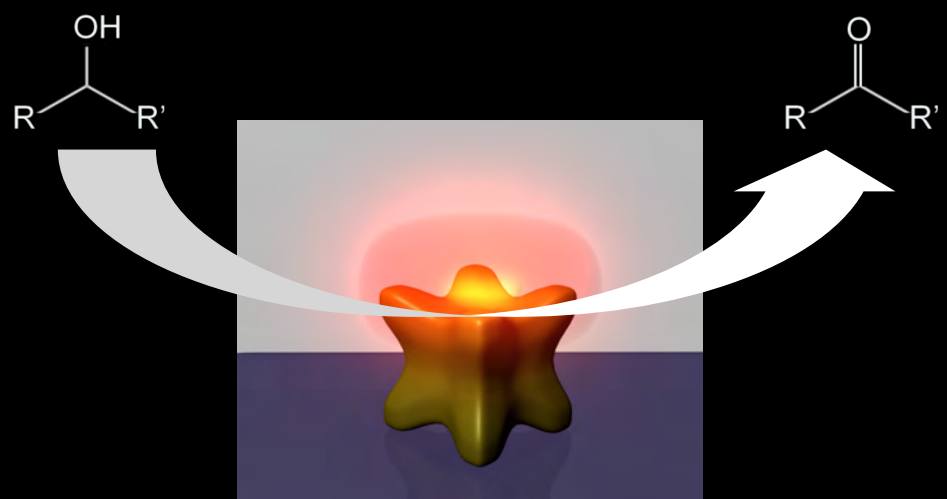




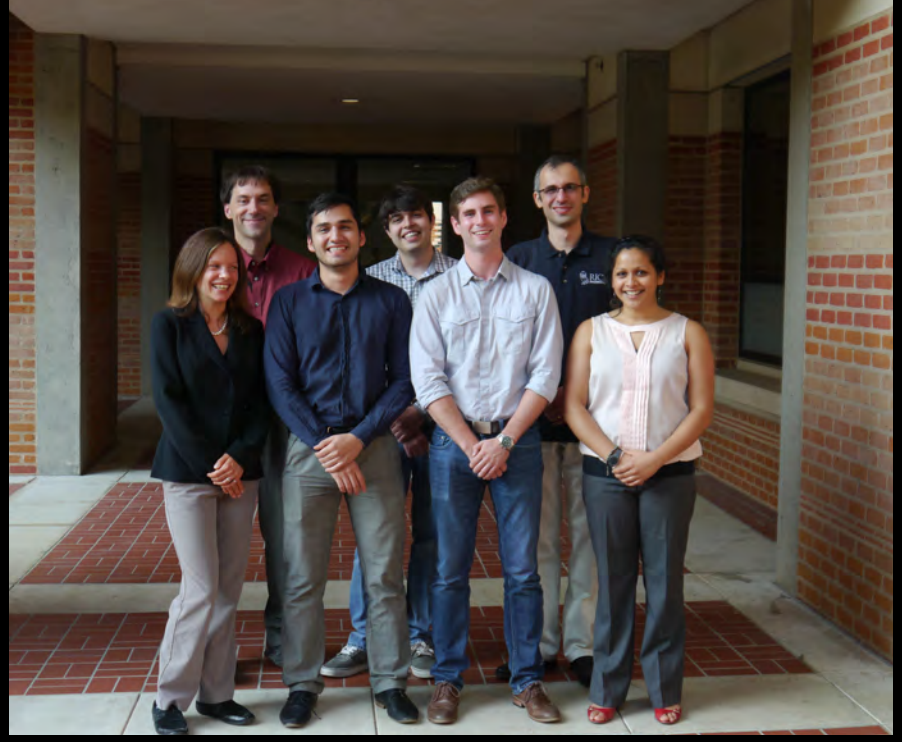
Photocatalysis / Plasmon-enhanced catalysis



THANKS!

Collaborators on Triangles, Al Plasmonics & Octopods

Prof. Naomi Halas (Rice)
Mike McClain (Rice)
Prof. Jill Millstone (U. Pitt.)
Patrick Straney (U. Pitt.)
Prof. Sara Skrabalak (Indiana)
Prof. Paul Midgley FRS (Cambridge)
Dr Sean Collins (Cambridge)
Dr Rowan Leary (Cambridge)
Dr Christopher DeSantis (Indiana/Rice)
Dr Nicolas Large (Northwestern U.)
Prof. Rafal Dunin-Borkowski (Juelich)



Group (L→R): Emilie Ringe, Anthony Stender, Eduardo Villarreal, Ryan Newell, **Dayne Swearer**, **Sadegh Yazdi**, **Anjli Kumar**

Affiliations

SMALLEY INSTITUTE

RICE IBB Institute of Biosciences and Bioengineering

LANP LABORATORY FOR NANOPHOTONICS

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NSF

ACS PRF

RICE