AVT-340 Research Workshop on Preparation and Characterization of Energetic Materials

A NEW CONCEPT FOR REACTIVE ALUMINUM NANOPARTICLES AS NOVEL ENERGETICS VIA ATMOSPHERIC PLASMA SURFACE ENGINEERING

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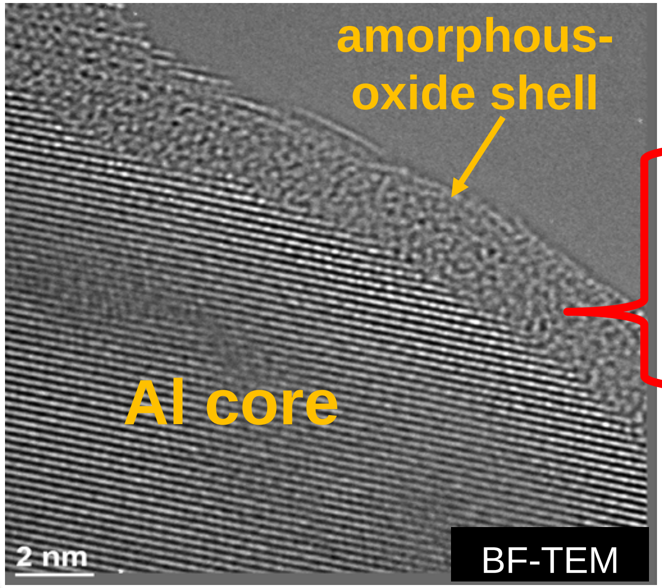
DEVCOM U.S.ARMY

2-4 & 9-11 February 2021

ALUMINUM FOR ENERGETICS

Heat of combustion 31 kJ/g (TNT=14.5 kJ/g)

$Al_{(s)} + O_{2(g)} \rightarrow Al_2O_{3(S)}$

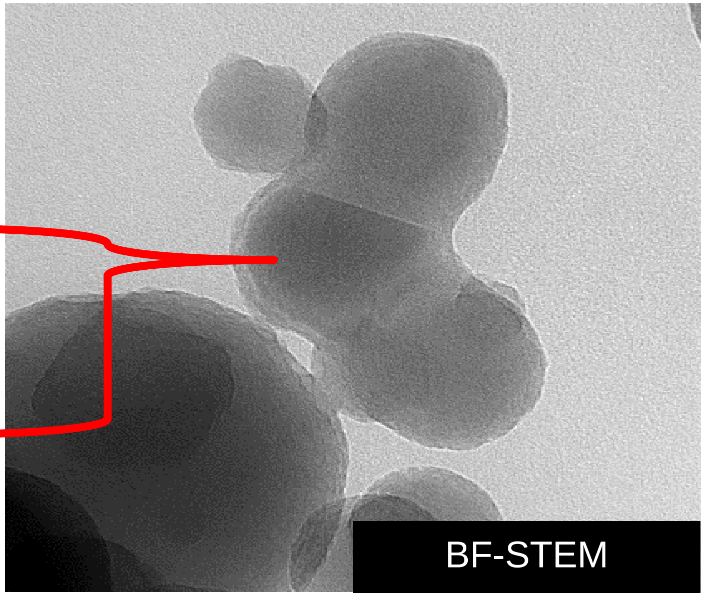


The oxide shell consumes a significant volume when size reduces

- ***Increased active Al content by reducing the shell conent***

nano-size (n-Al)

+ Potential fast energy release
+ High surface area to volume ratio



Agglomeration reduces reactivity

- ***Improved dispersity in formulation by surface coating***

Major questions

- Can ALL the energy be released?
- Can all the energy be released QUICKLY?

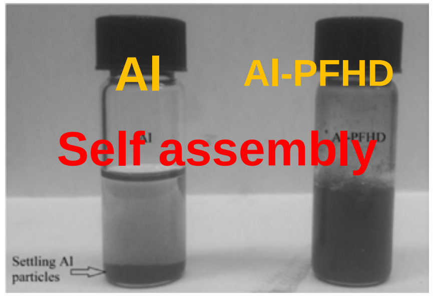
Approach: Eliminate/minimize shell thickness

BACKGROUND: PREVIOUS WORK ON ALUMINUM

Production

Functionalization by mixing commercial nAl with different oxidizers

- Aerosol
- Electrospray
- Laser ablation
- Mechanical Ball milling
- Sonication
- Pressing

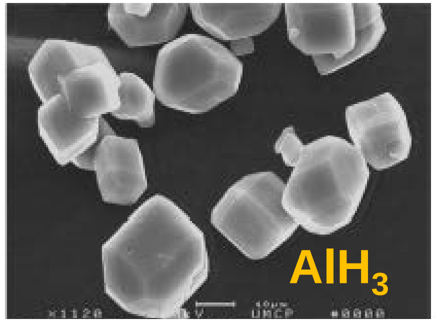


MN Vello, Combustion & Flame 2018

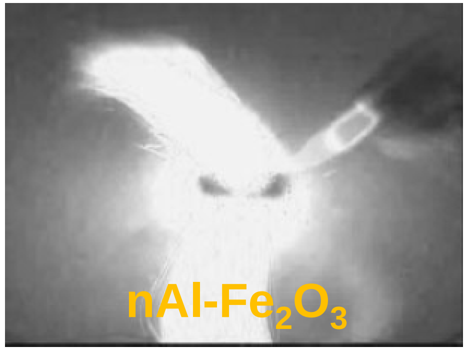
SC Thuot et al., SCCM 2009

Characterization & Testing

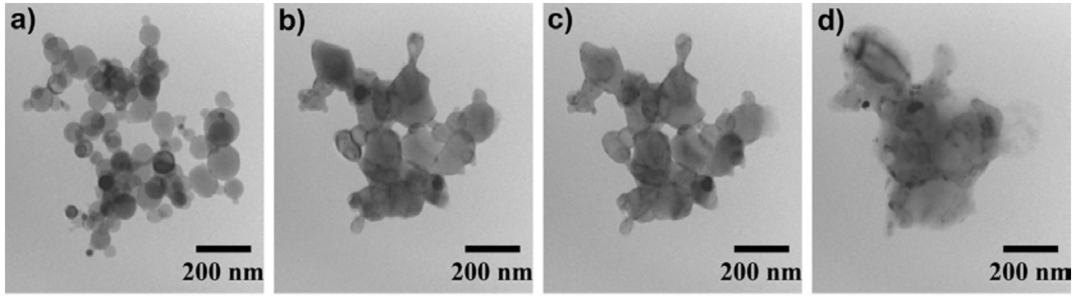
- SEM, (dynamic) TEM, DSC
- Ignition, combustion, Flame speed



Young et al., J Propulsion & Power 2014



Kim et al., Adv. Mater 2004



Egan et al., JAP 2014

- **Limited reports on detonation results due to need for large sample quantities**
- **Plasmas provide tunable flexibilities in controlling material properties and energetic output!!**

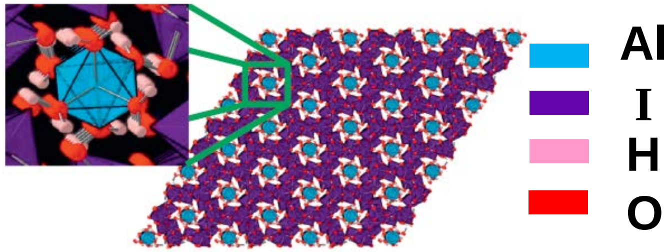
ENERGETIC OXIDIZING SALT-AIH

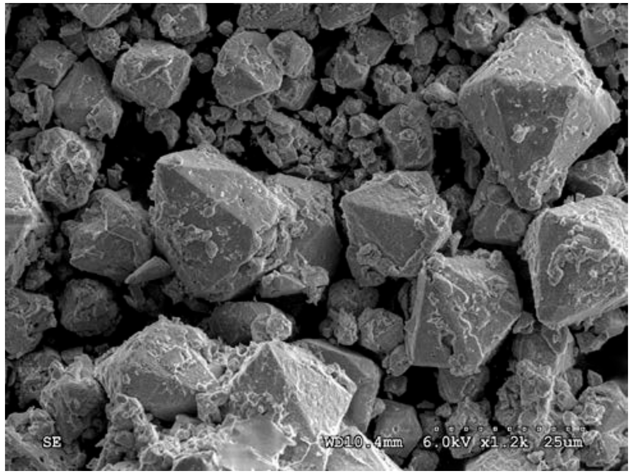
Prof. Pantoya has developed AIH & Al@ AIH via solution synthesis

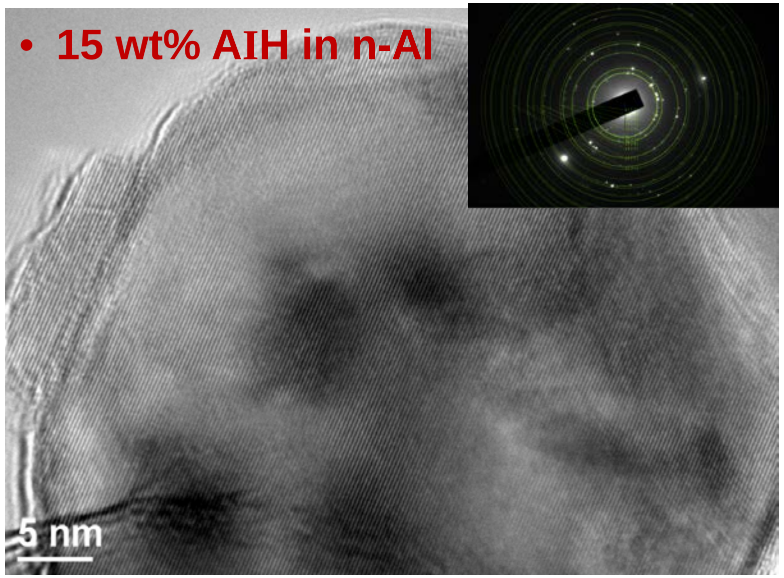
- Show the promise of enhanced reactivity
- ARL characterization demonstrated the high crystallinity of Al@AIH

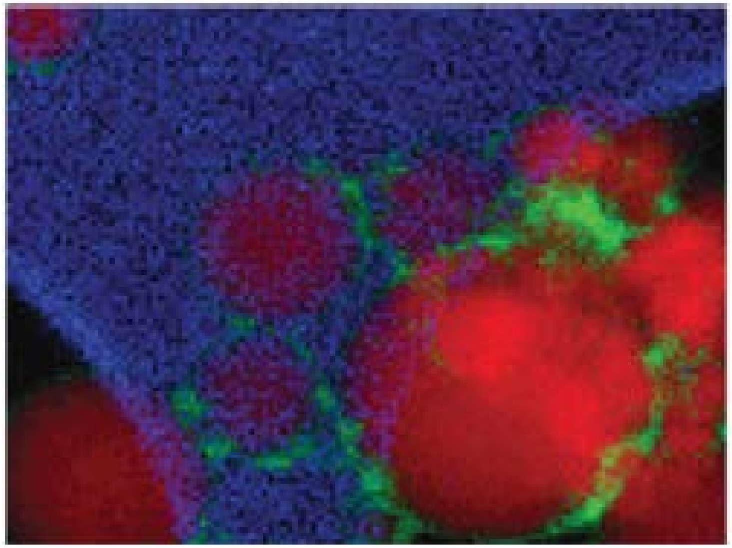
Prof. Michelle Pantoya
Texas Tech University, USA

AIH: Aluminum Iodate Hexahydrate
$Al(IO_3)_3(HIO_3)_2(H_2O)_6$



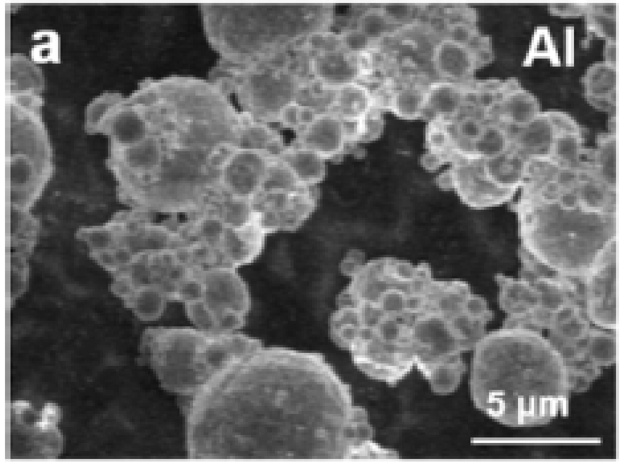


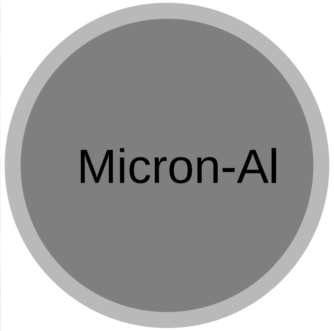




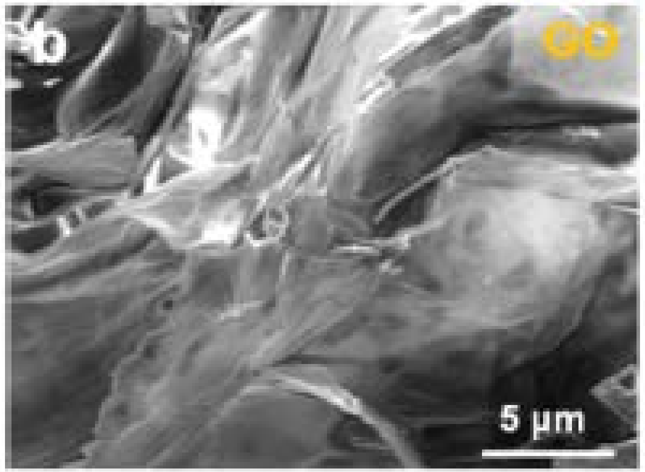
- DK Smith et al., Thermochimica Acta 641 (2016) 55.
- DK Smith et al., J Phys Chem C 121 (2017) 23184.
- Shancita et al., J Phys Chem C 123 (2019) 15017

ENERGETIC Al/GO

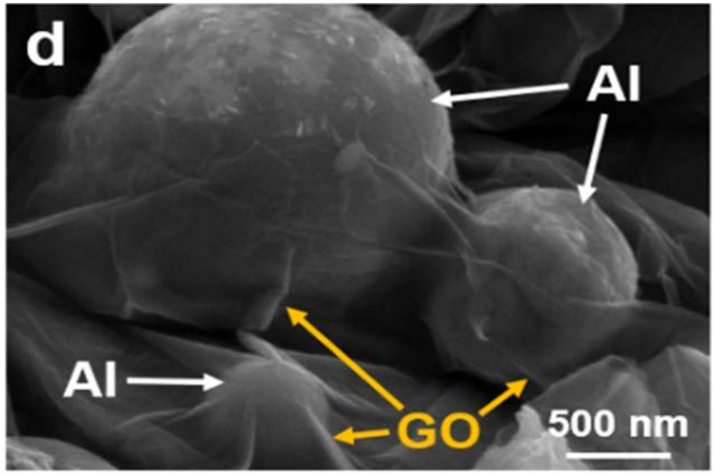


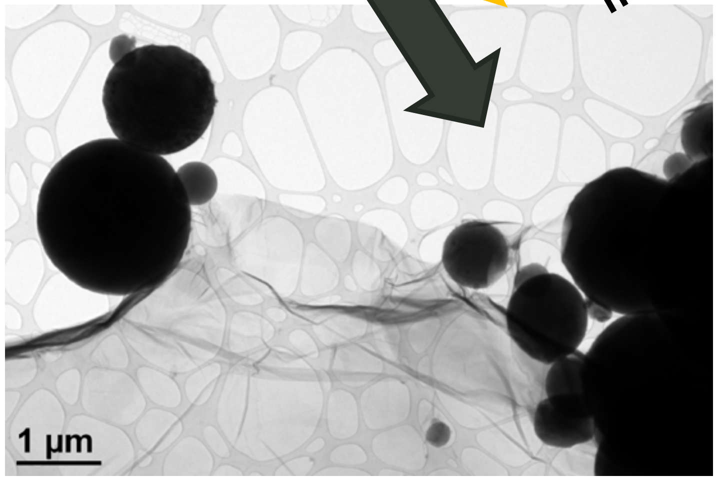


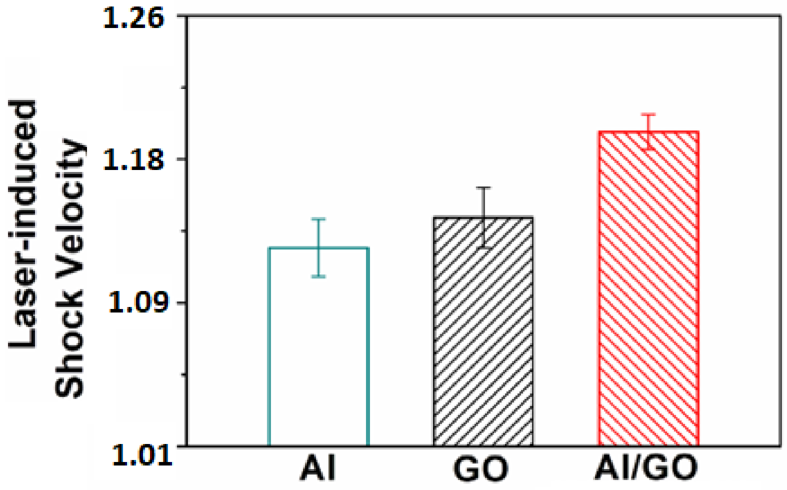
Prof. Xiaolin Zheng
Stanford Univ. (US)



Ultrasonic mixing







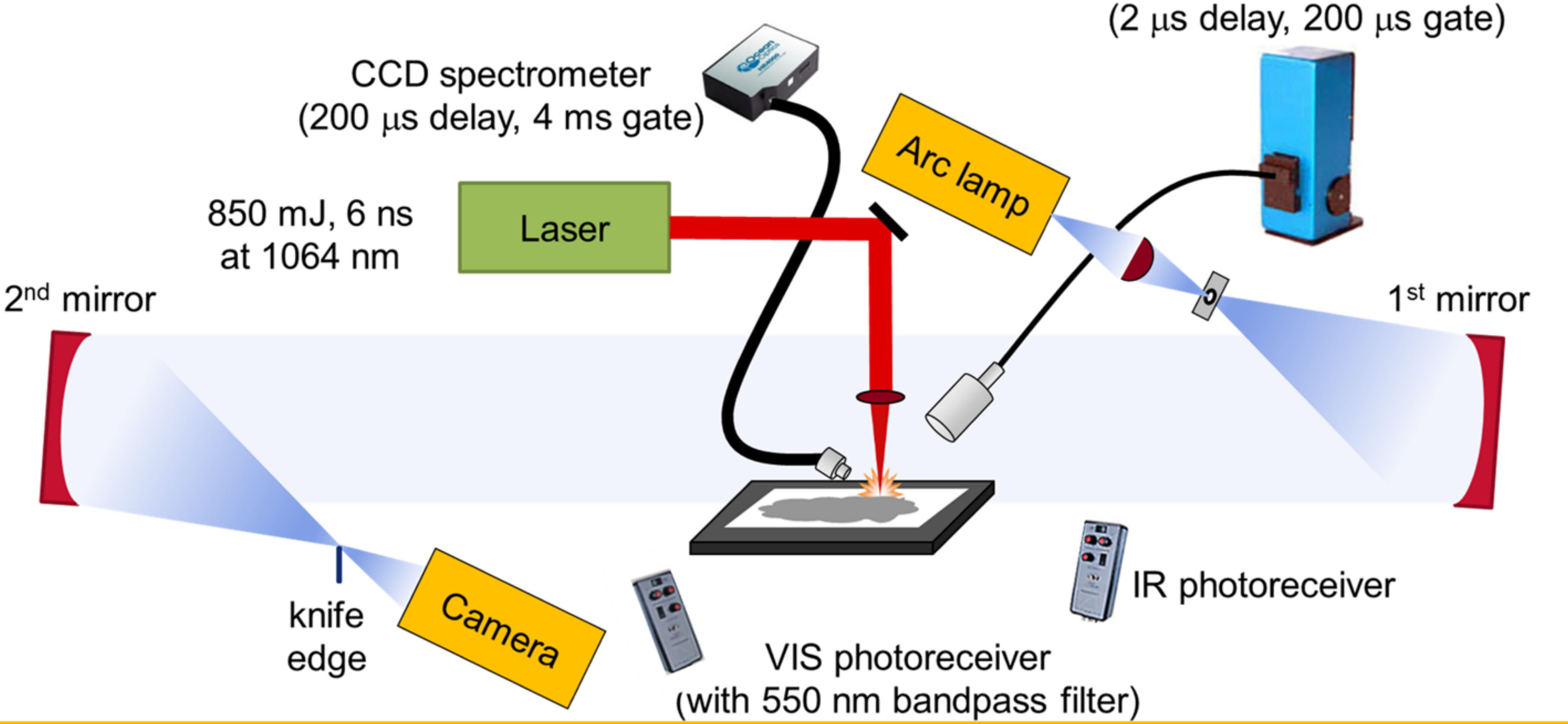
[Y Jiang, et al. ACS Nano 12 (2018) 11366-1375]

Enhanced laser shock velocity of Al/GO at microsecond scale

LASER-INDUCED AIR SHOCK FROM ENERGETIC MATERIALS (LASEM)

- **Measure the fast energy release at the microsecond timescale**
- **Measure the blast effects at the millisecond timescale**

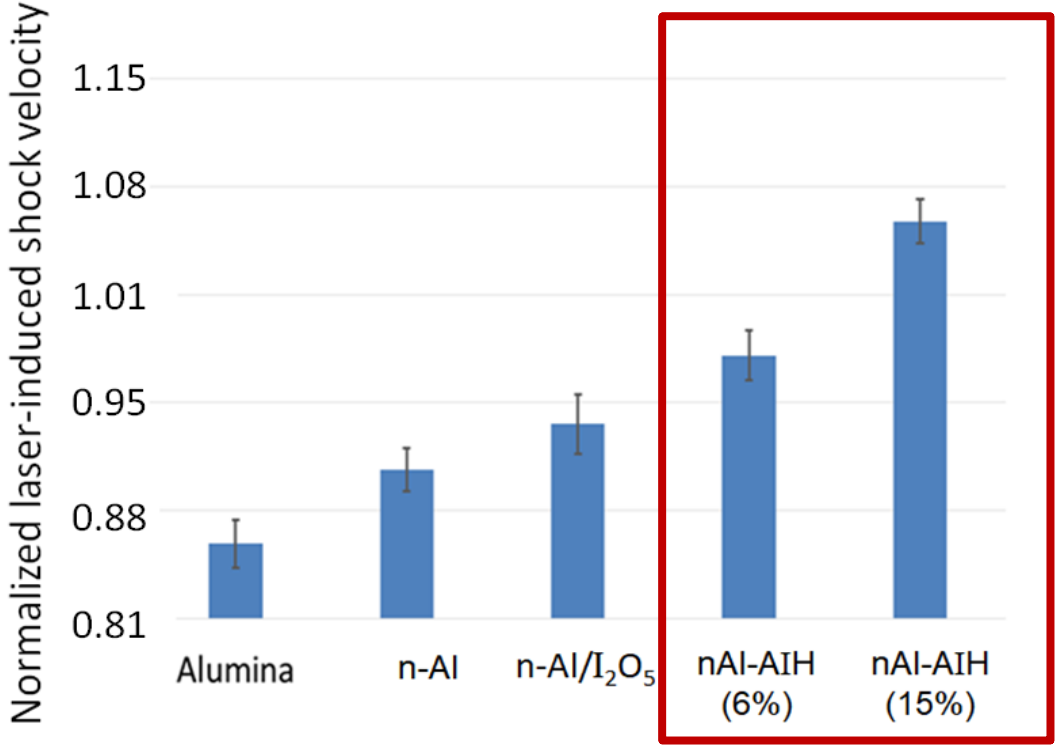
JL Gottfried, Phys Chem Chem Phys, 16 (2014) 21452-21466

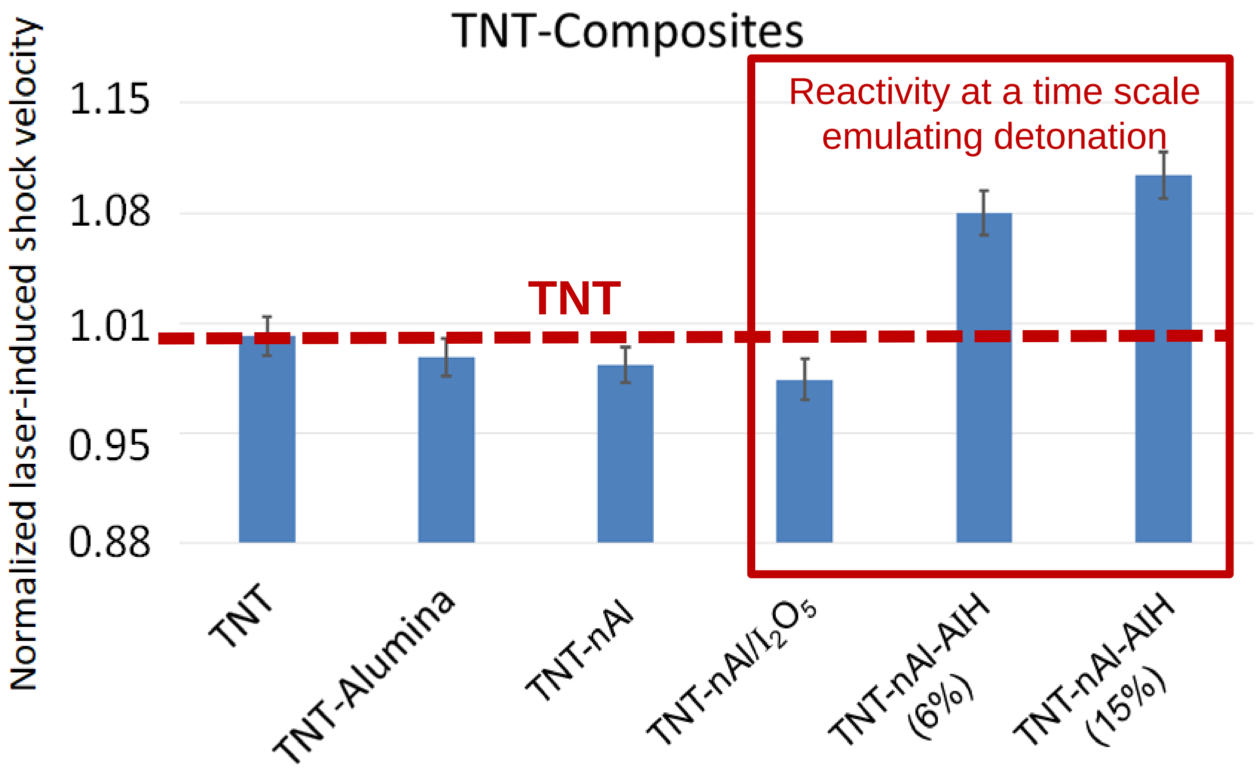


ENHANCED REACTIVITY OF Al@AlH COMPOSITES

Only 15% AlH in commercial n-Al increases TNT performance by 30%! (n-Al:TNT=1:4)

- Shows the potential of AlH as oxidizer and possible further enhancement with plasma-treated n-Al
- **Hypothesis: He and Ar Plasma treatments *may* make Al@AlH even more energetic!!**

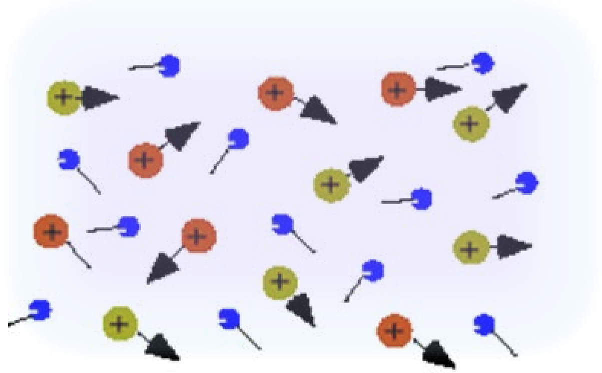




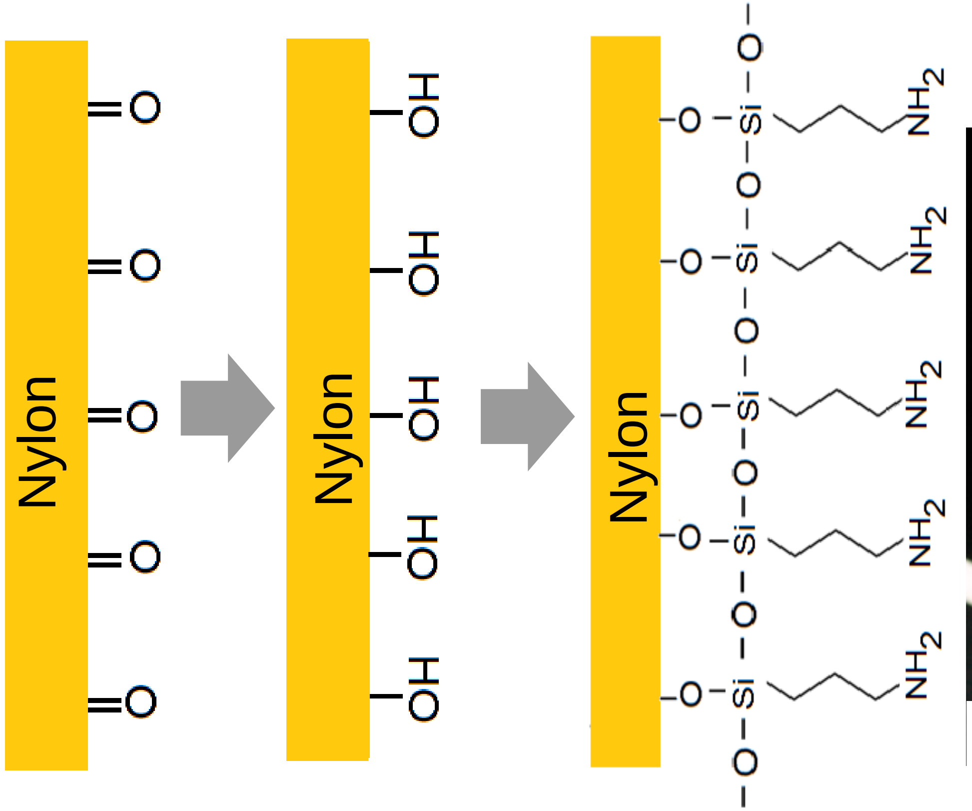
[JL Gottfried, DK Smith, CC Wu, ML Pantoya, Scientific Reports 8 (2018) 8036]

PLASMAS COUPLE ENERGY AND MATTER

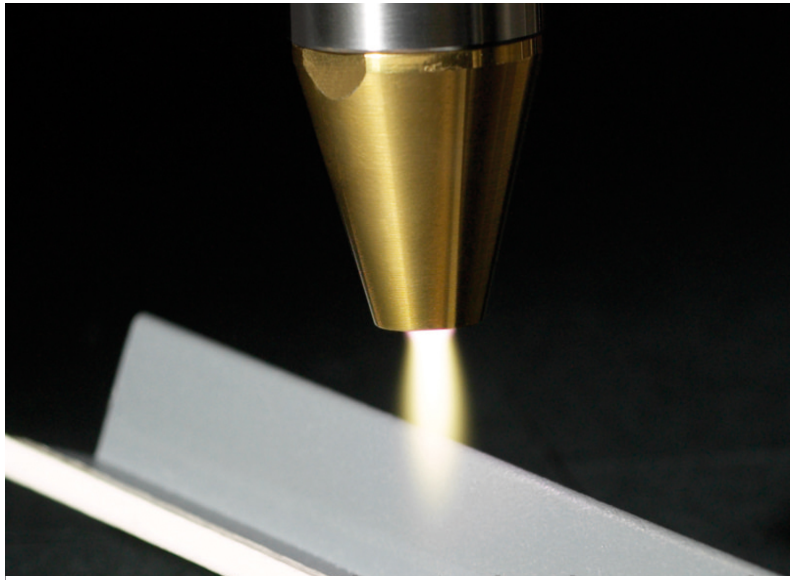
Energized medium consists of ions, radicals, electrons



- Surface treatment/grafting

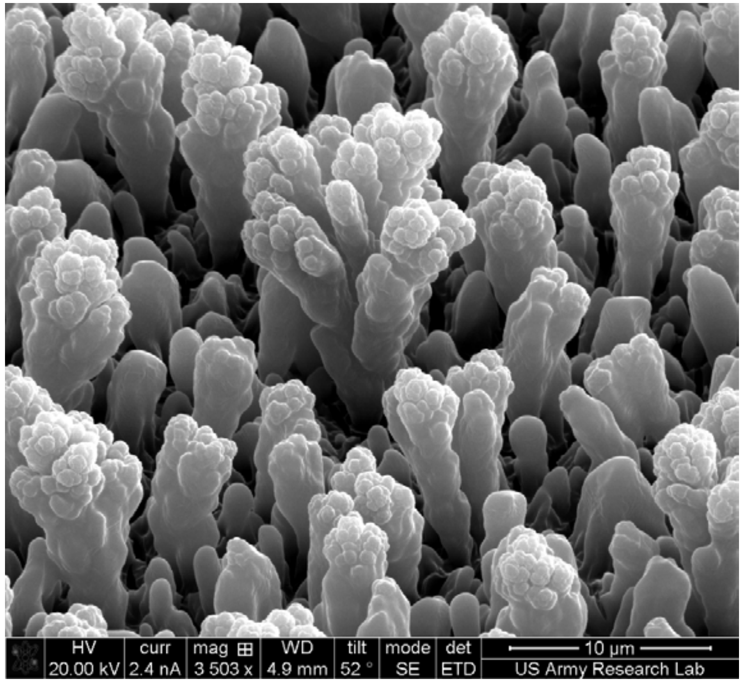


Plasma cleans bulk Al surface
Remove the surface oxide



dynetechnology.co.uk

Extended solids formed via PECVD



[C-C Wu, 2015 MRS Fall Meeting]
[AA Bujanda, C-C Wu, JD Demaree, EJ Robinette, 2015 TMS Proceedings]

OBJECTIVE

Produce and ***OPTIMIZE*** nAl with highest energy content & fastest energy release via controllable plasma experimental conditions, nano-scale characterization & lab-scale energetic tests

Plasmas

- Atmospheric dielectric barrier discharge (DBD) reactors
- Argon or helium plasma
- Reactor with or w/o arcing
- 10 or 30 min plasma duration
- Commercial nAl

Characterization

- Nanoscale: TEM, XPS, XRD, FTIR, MD modeling
- Thermoanalytical: DSC/TGA
- Lab-scale test: LASEM
- Small-scale detonation test

2nd step-Plasma

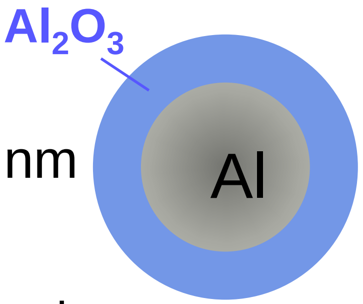
Wet chemistry mixing

- $I_2O_5\ _{(s)} + H_2O\ _{(aq)} \rightarrow HIO_3\ _{(aq)}$
- Plasma-treated nAl particles

- Carbonaceous coating
- Reactive nAl@C

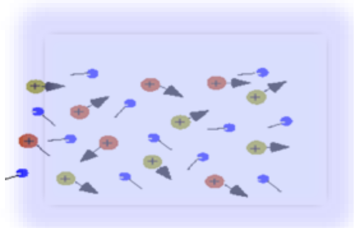
ARL PLASMA APPROACH

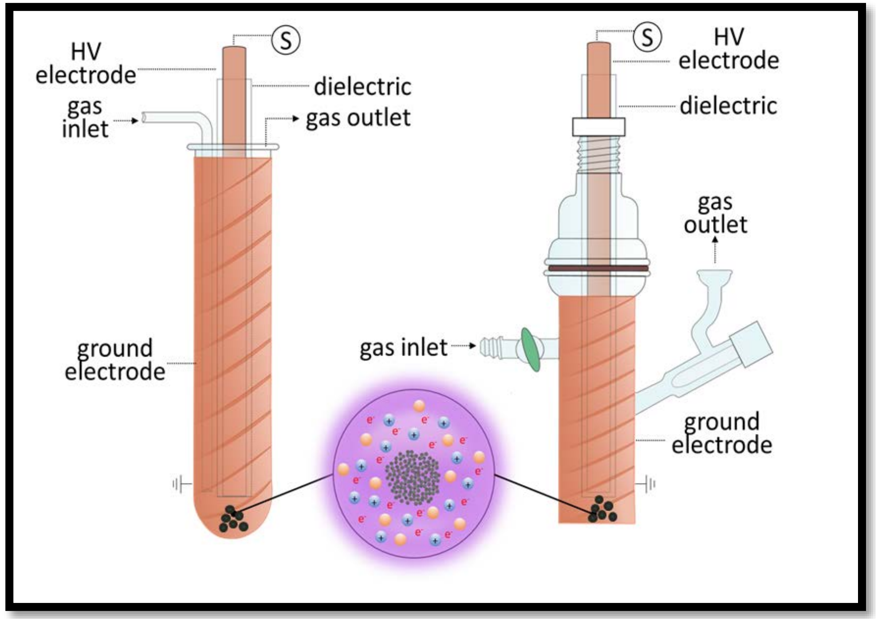
Step 1: Oxide Shell Reduction & Surface Modification

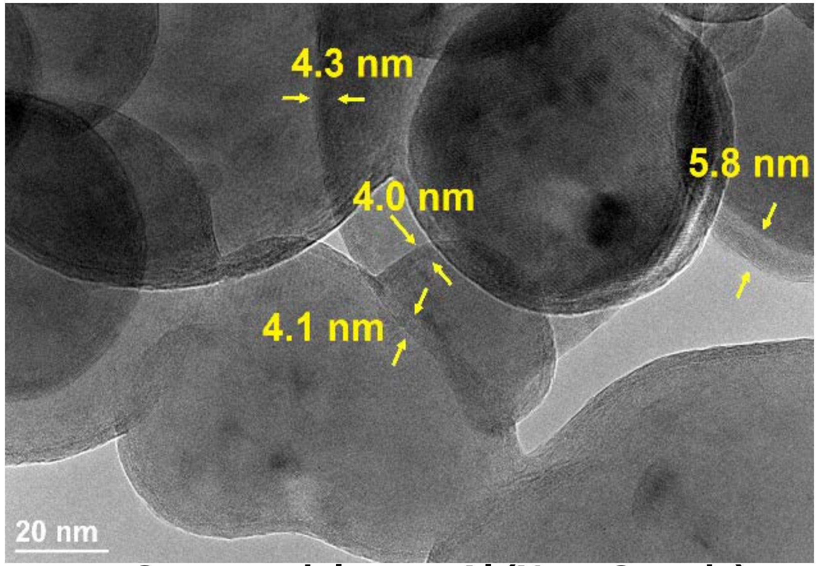


Al_2O_3 Shell: 4-6 nm

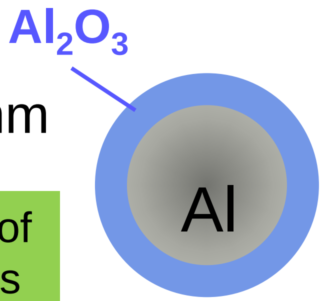
- 1 SLPM He, Ar
- 10 or 30 min duration
- 25 W





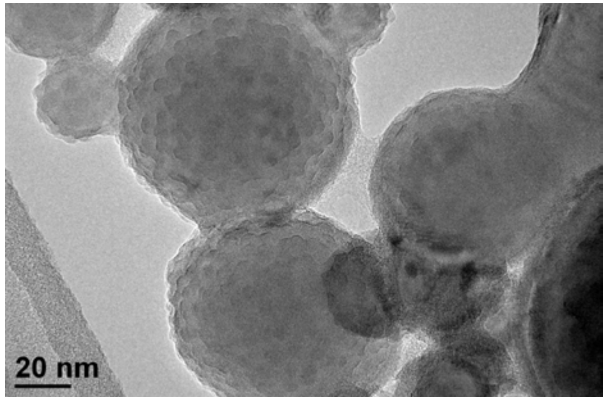


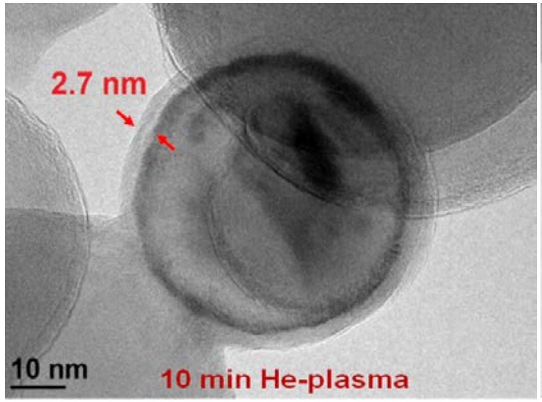
Commercial nano-Al (NovaCentrix)

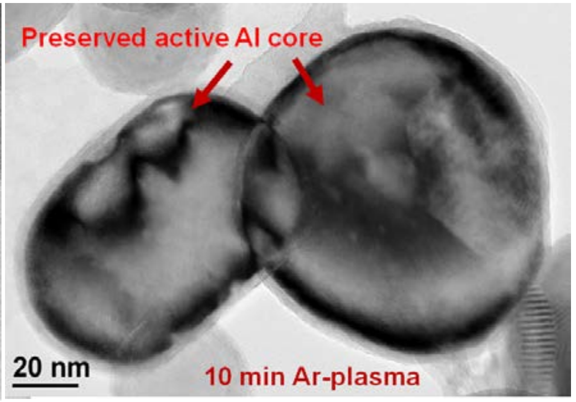


Al_2O_3 Shell: ~3 nm

40% avg. reduction of oxide shell thickness







[C-C Wu*, KK Miller, SD Walck, ML Pantoya, MRS Advances 2019, DOI:10.1557/adv.2019.159]
[Miller, ARL Summer Symposium, 2018]

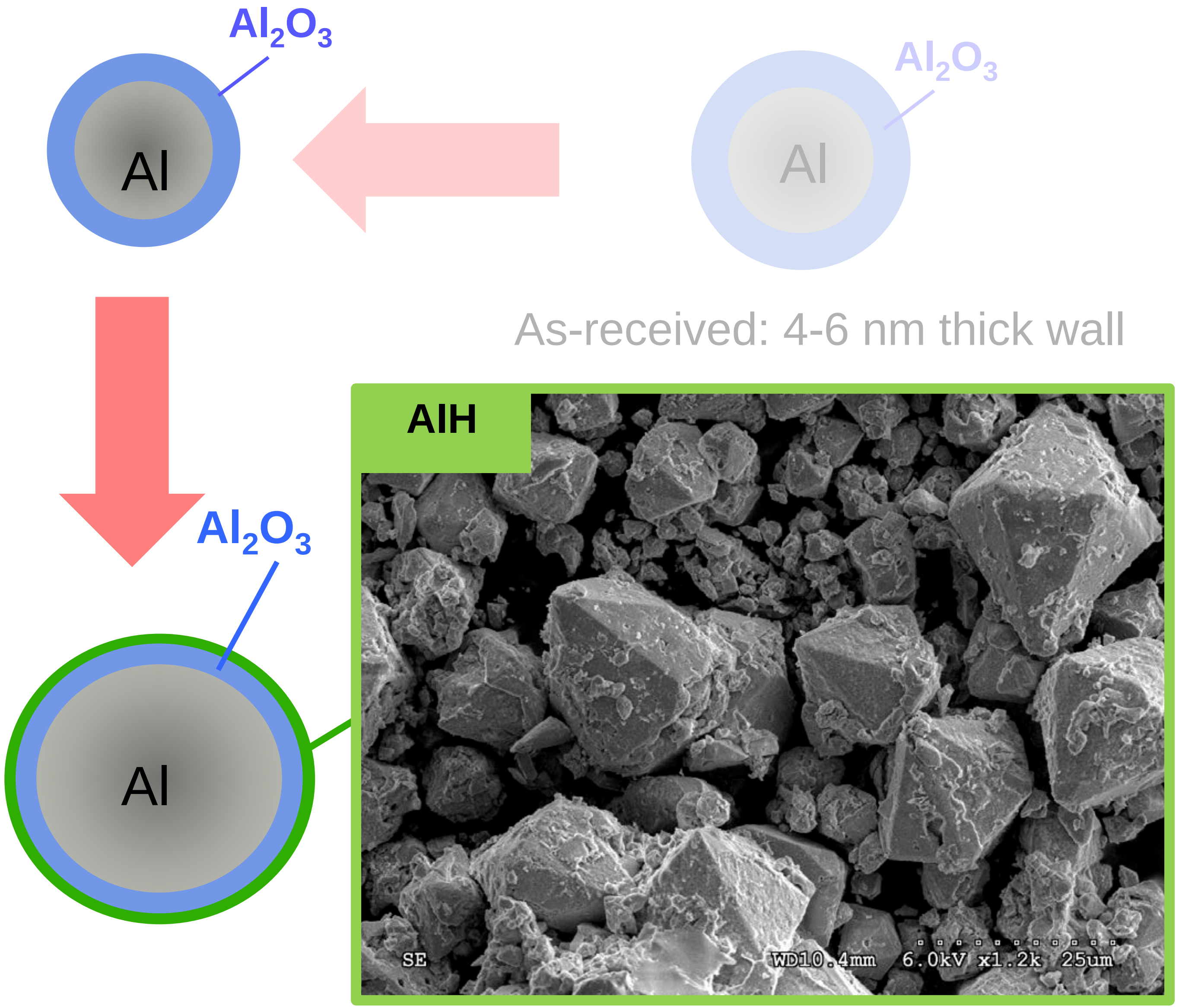
ARL PLASMA APPROACH (CONT'D)

Step 2: Hand mixing of plasma treated nAl with HIO_3 (aq)

Avg. 40% reduced Al_2O_3 Shell thickness from Step 1: ~ 3nm

Iodate solution HIO_3 (aq)

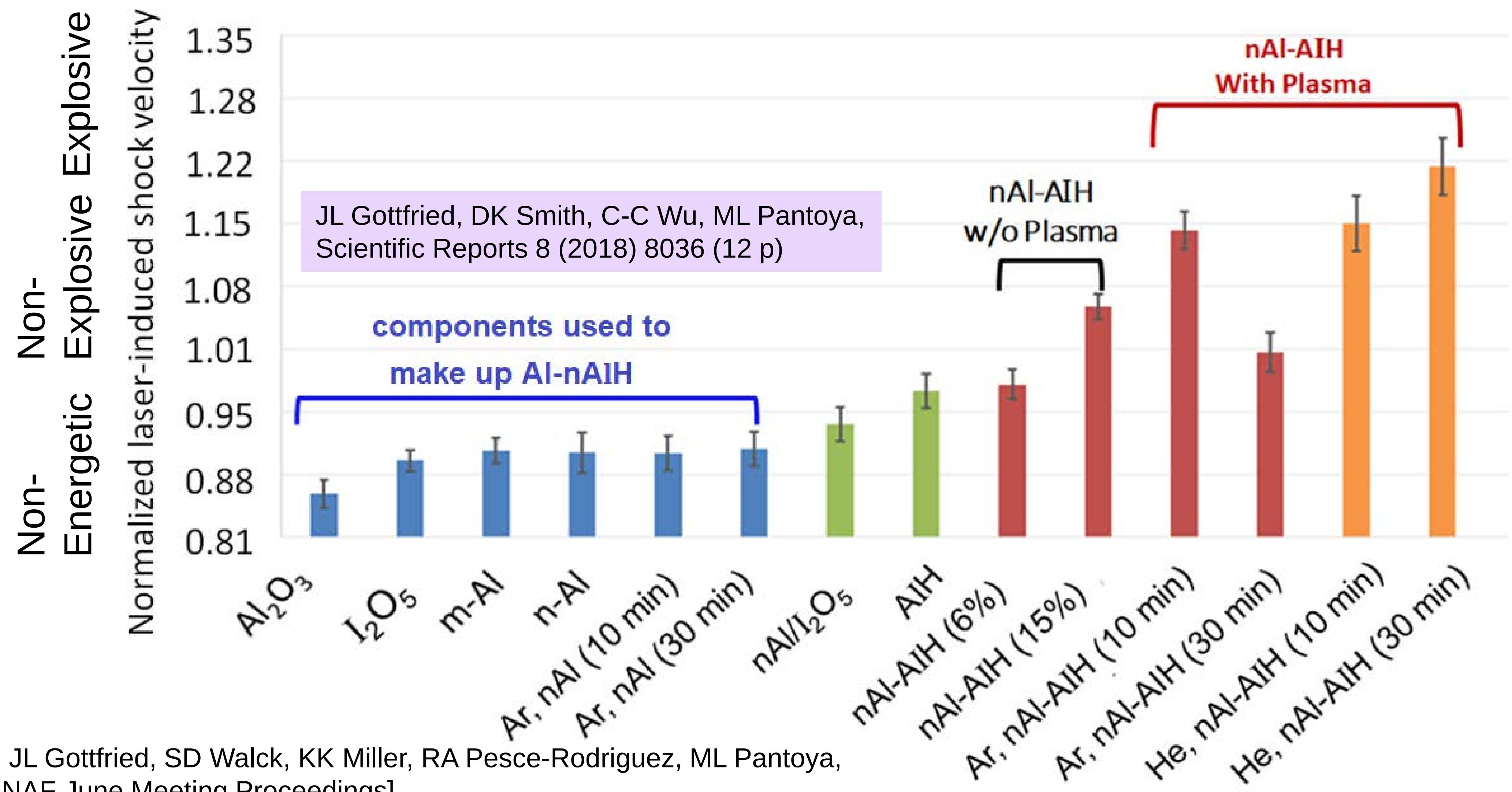
- nAl: I_2O_5:H_2O=1:1:2.5
- Hand mixing



Al_2O_3 Shell: even thinner (~1-2 nm)

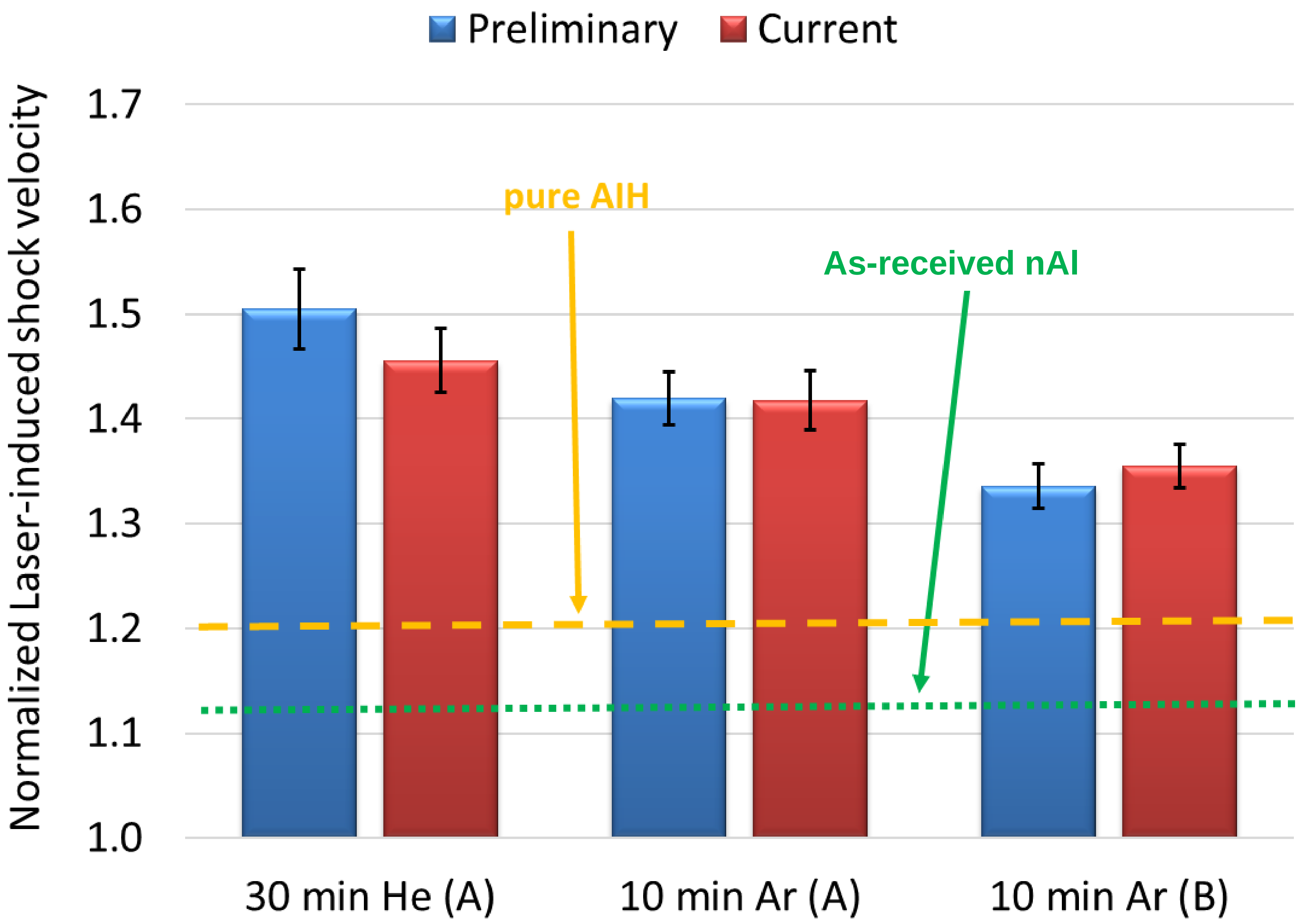
ENHANCED ENERGY RELEASE

LASEM experiments performed by Dr. Jennifer L. Gottfried



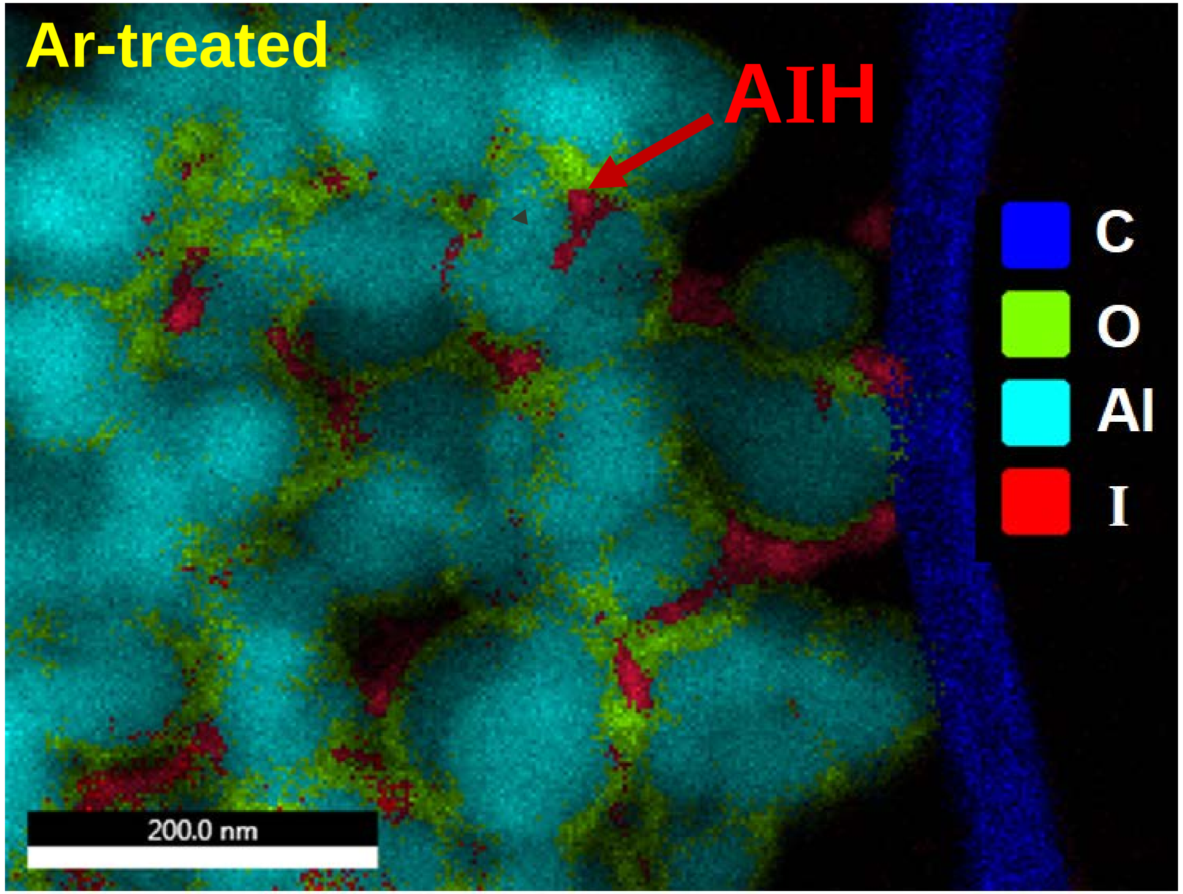
[C-C Wu, JL Gottfried, SD Walck, KK Miller, RA Pesce-Rodriguez, ML Pantoya, 2019 JANNAF June Meeting Proceedings]

REPRODUCIBLE ENHANCED ENERGY RELEASE

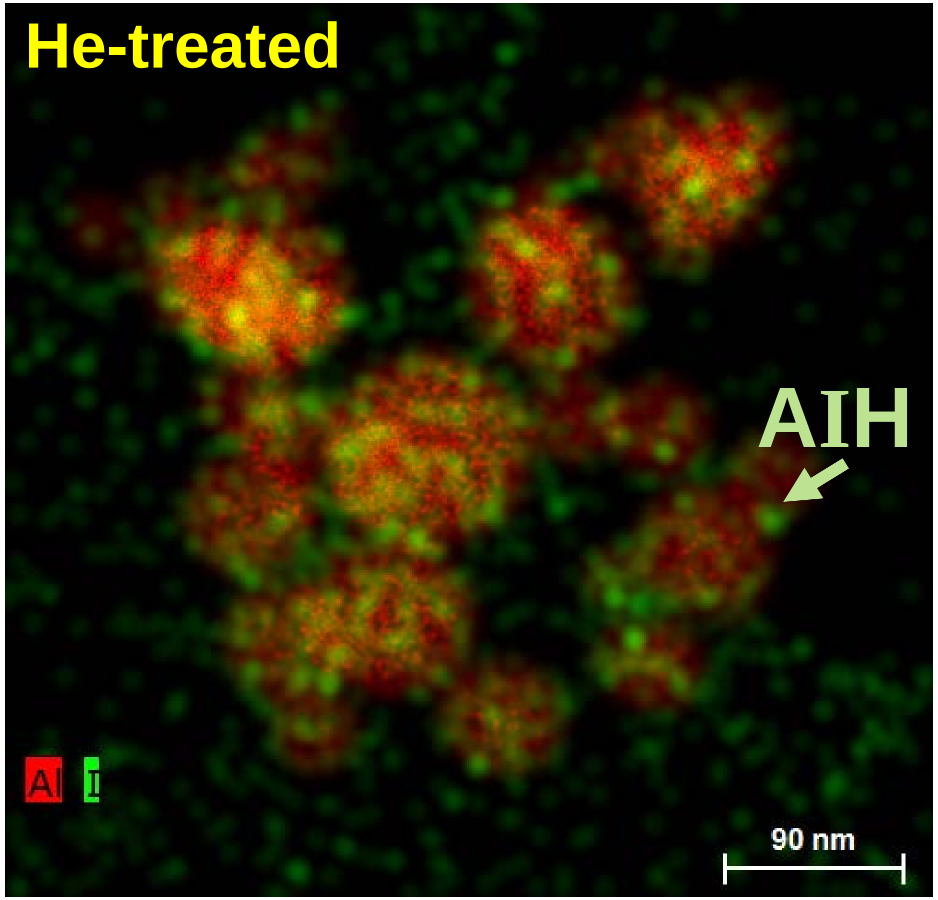


ELEMENTAL MAP

Different Iodine Distribution between Ar and He Plasma-treated nAl-AIH



STEM XEDS Map @ ARL/WMRD JEOL 2100F TEM



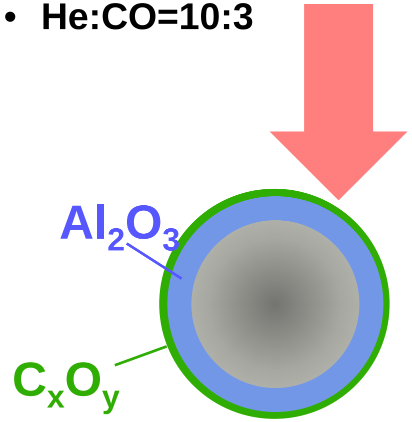
AC-STEM XEDS Map@CNM/Argonne National Lab
Talos Thermo Fisher F200X TEM

[Miller et al., Combustion and Flames 206 (2019) 211]

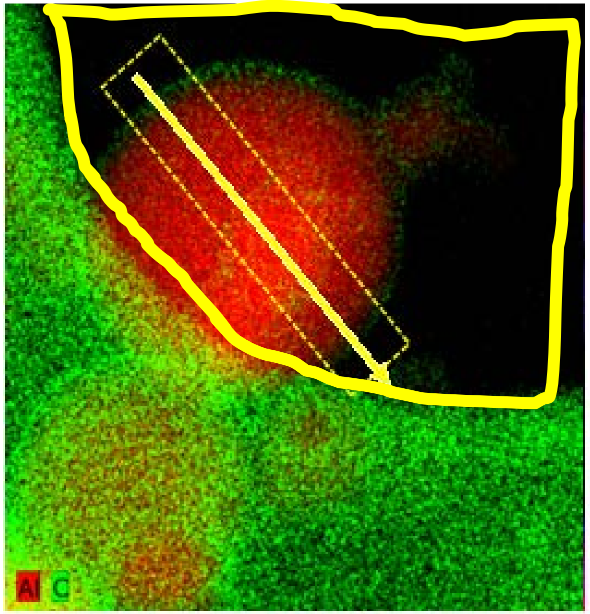
ATMOSPHERIC PLASMA SYNTHESIS OF Al@C

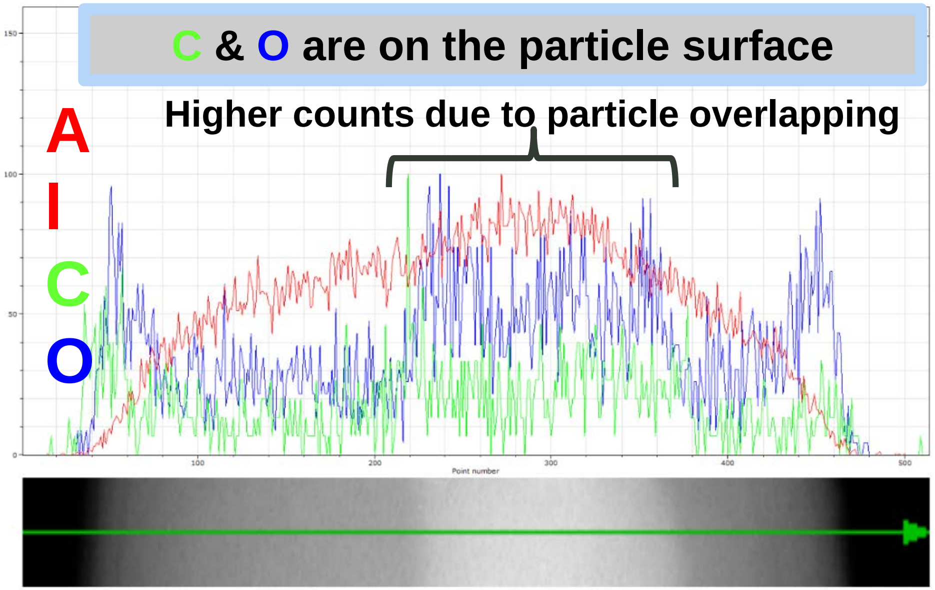
Step 2: Addition of carbons

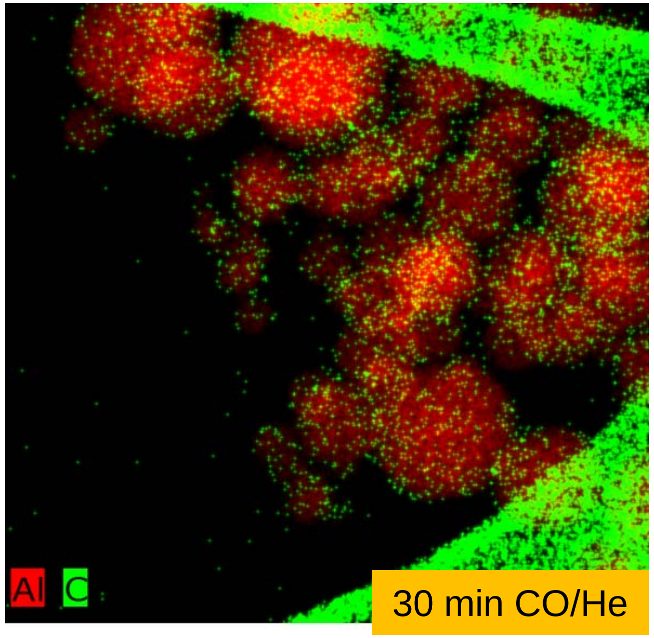
- **10, 30, 60 min treatment durations**
- **He:CO=10:3**



Al_2O_3 Shell: even thinner (~1-2 nm)



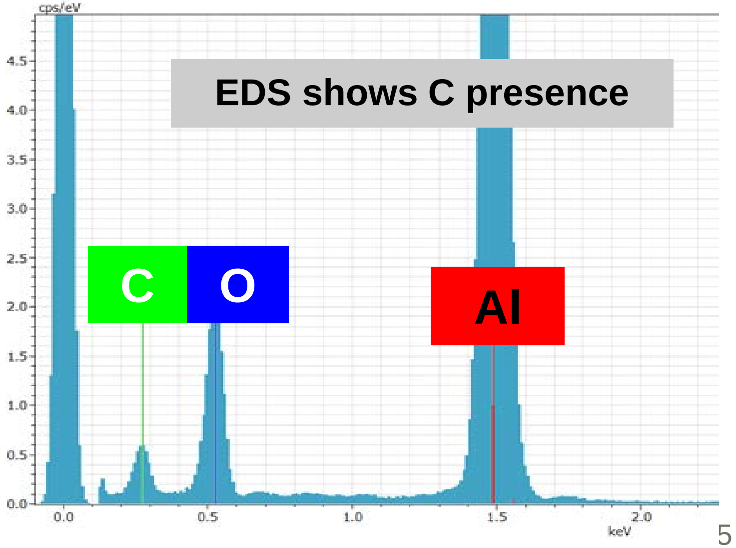




Elemental map confirms C

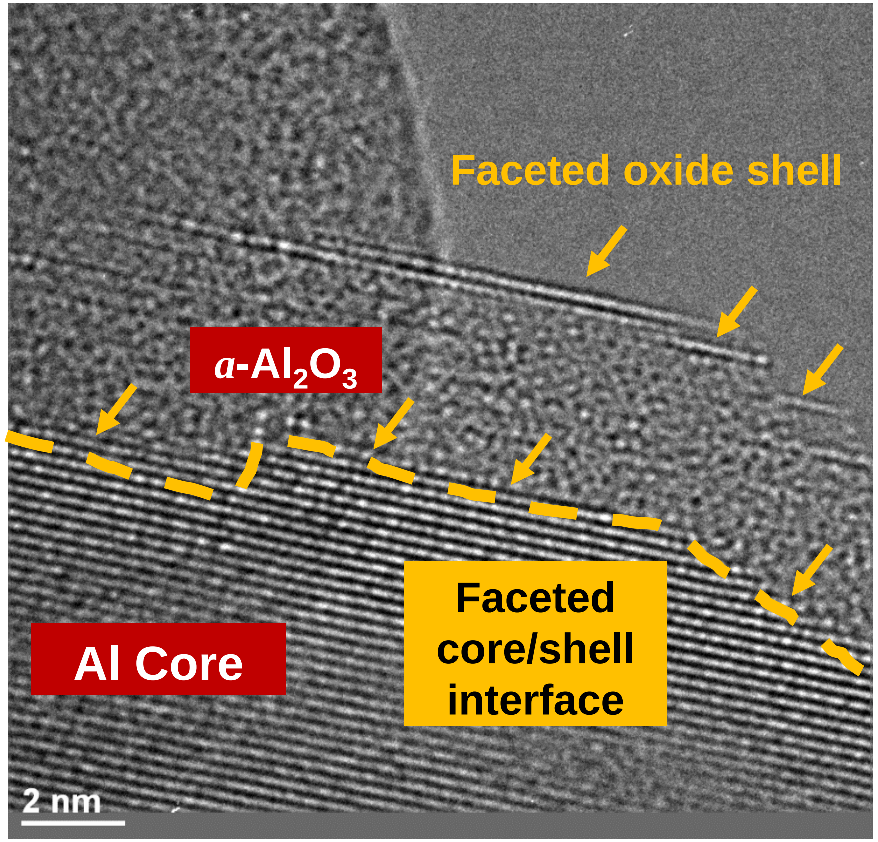
- Wu et al., MRS Advances 4, (2019) 1589
- Wu et al. ARL-TR-9027 (Aug, 2020)
- Wu et al., 2021 JANNAF Virtual Meeting Proceedings
- Wu et al., J. Appl. Phys. (in press)

STEM X-ray maps were obtained using Talos FEI TEM (Argonne National Lab)

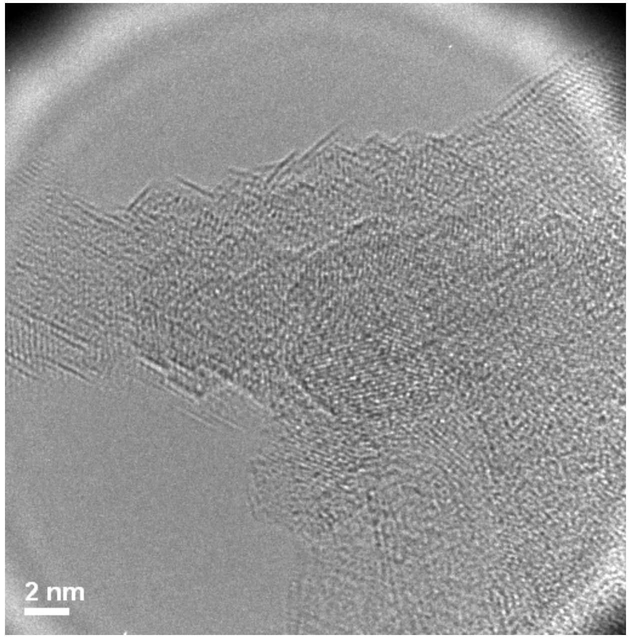


CHARACTERIZATION OF PLASMA-PRODUCED Al@C: HRTEM

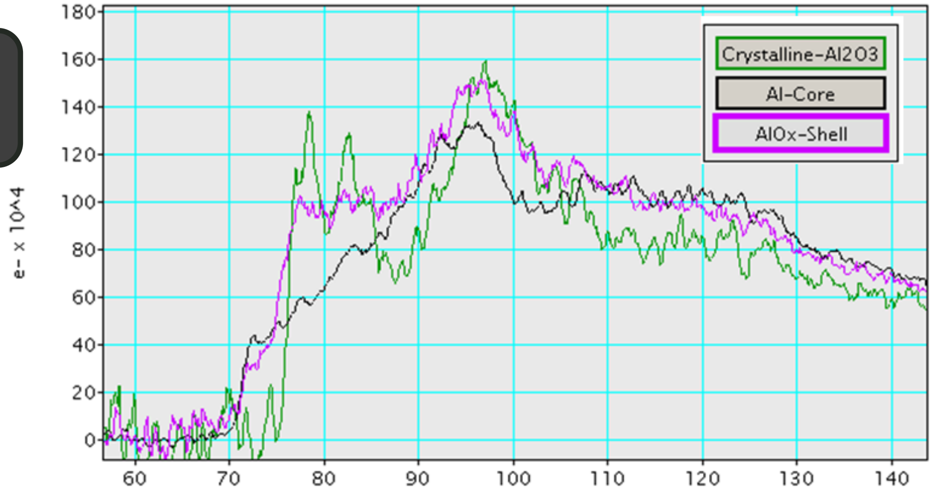
Morphological changes of Al_2O_3 shell

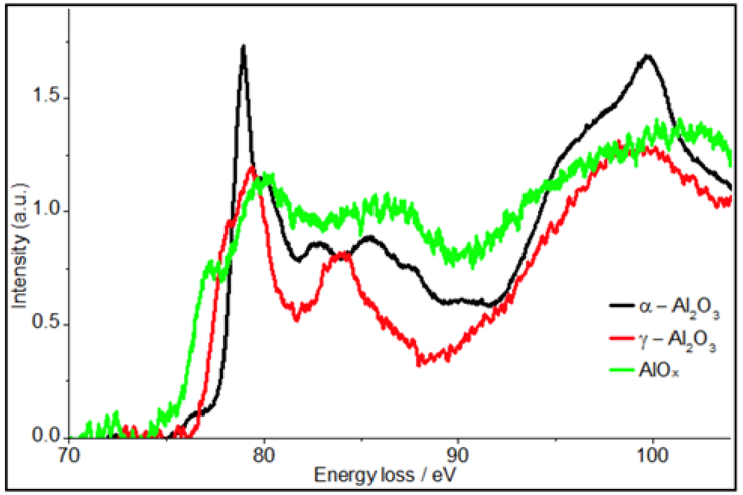


EELS confirms formation of γ-Al_2O_3



[Fritz et al., 16th European Microscopy Congress 2016. doi: 10.1002/9783527808465.EMC2016.5049]

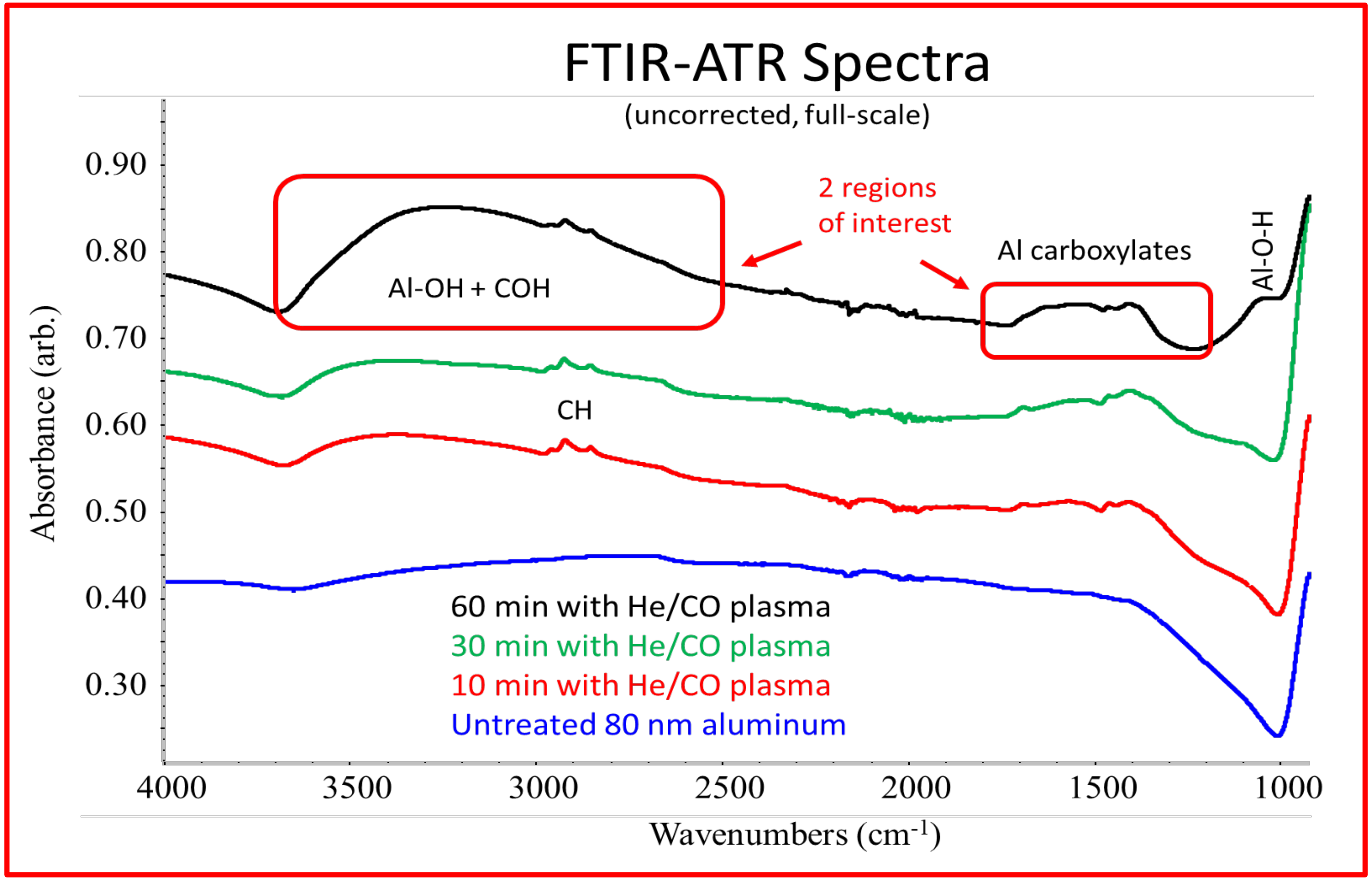




Similar morphology observed in ex-situ annealing and in-situ TEM heating

- HRTEM experiments were performed using ACAT FEI TEM (Argonne National Lab)
- ***Characterization data will be published in Wu et al., J. Appl. Phys.-Special Issue: Atmospheric Plasmas (2021, in press)***

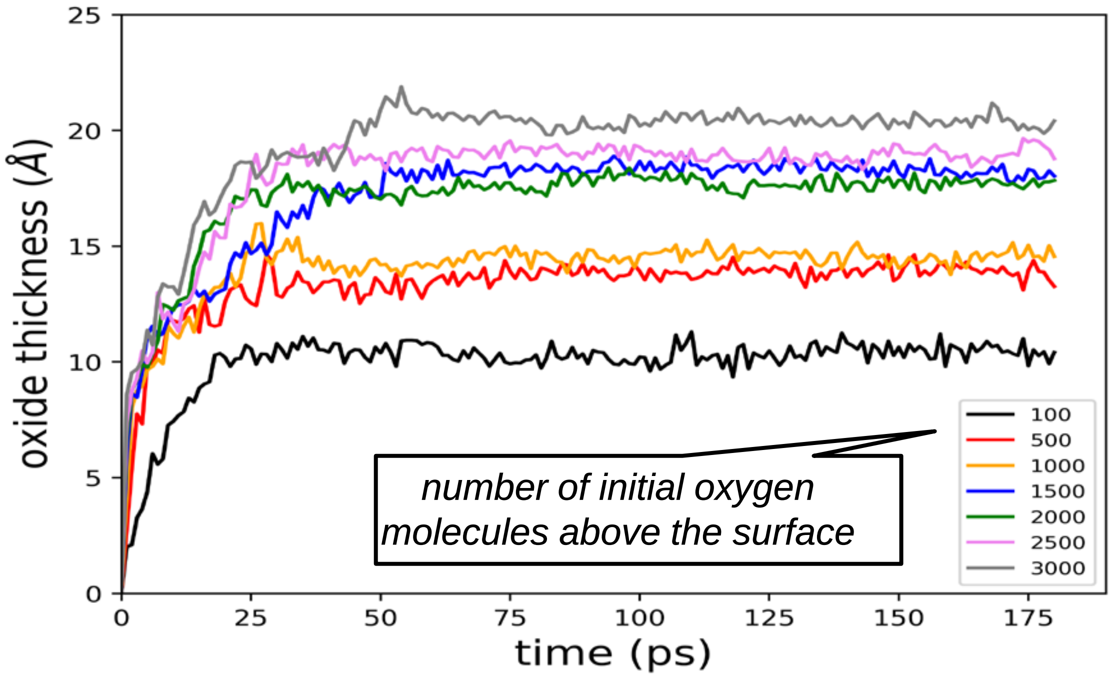
CHARACTERIZATION OF PLASMA Al@C: FTIR

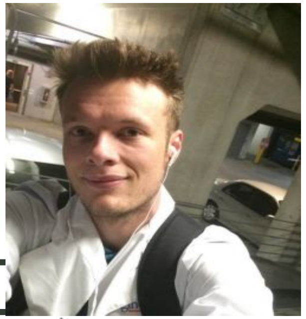


- Plasma- Al@C samples show features which do not exist in as-received nAl sample
- Al carboxylate peak increases with increased plasma treatment time and is most significant for 60 min sample

[Wu et al., J. Appl. Phys.-Special Issue: Atmospheric Plasmas (2021, in press)]

MOLECULAR DYNAMICS MODELING

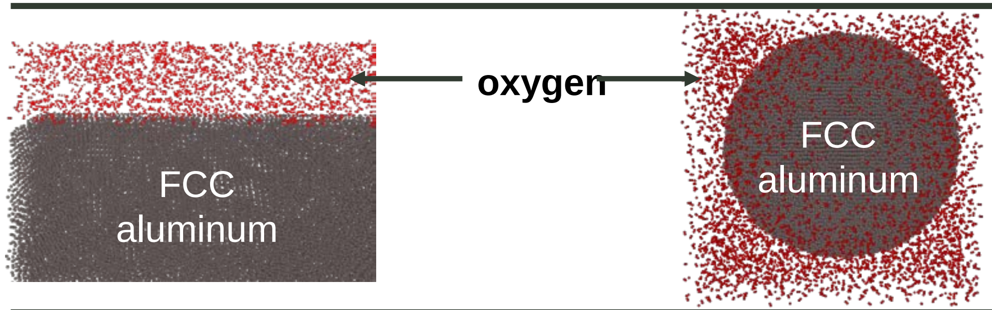




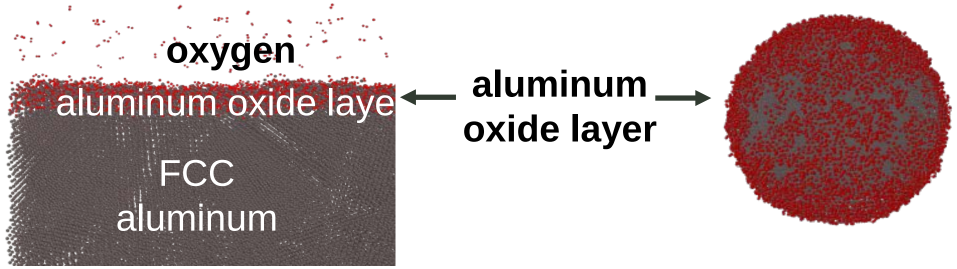
Dylan Anstine (Univ. Florida)

INITIAL SYSTEM

POPULATE WITH OXYGEN



OXIDIZE WITH MD

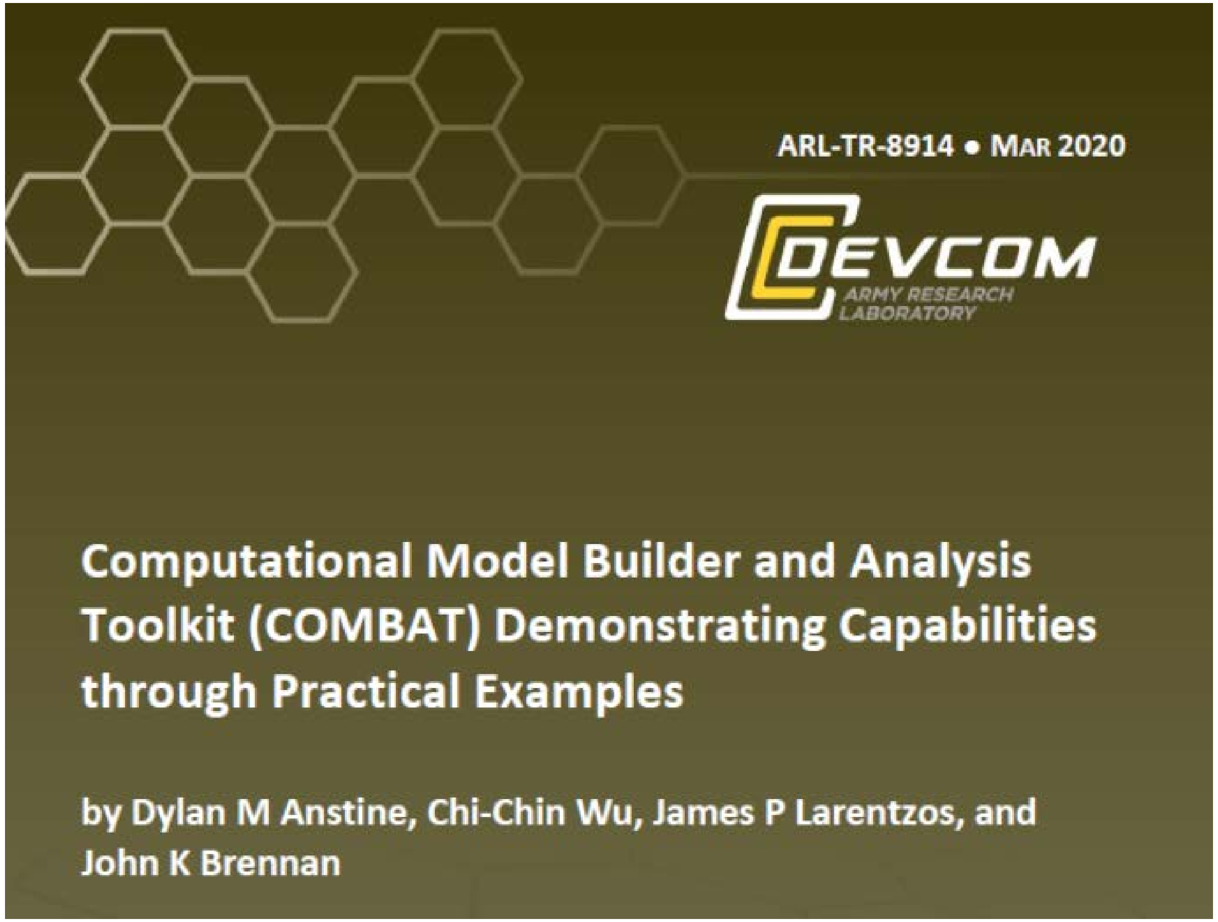


- Complex strong local electric fields remove oxygen or reduce oxygen binding to the Al core
- Loosely bound oxygen can be easily removed from energetic particle collisions
- Remaining oxygen in the core-shell model is the most thermodynamically favorable oxygen.

[Anstine, *et al.* ARL, ARL-TR-8914 (2020)]

CARBON COATING PREPARATION

2019: No coating


ARL-TR-8914 • MAR 2020

DEVCOM ARMY RESEARCH LABORATORY

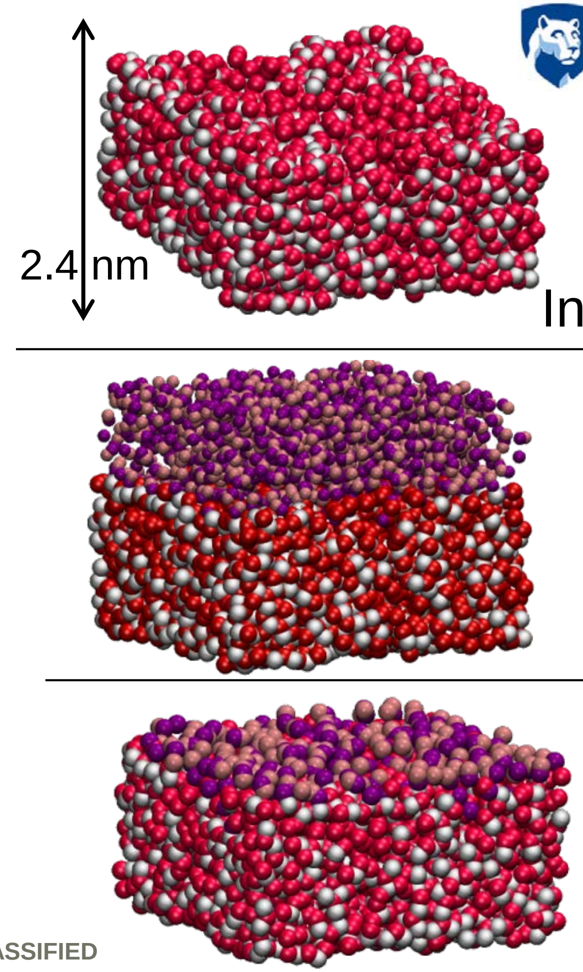
Computational Model Builder and Analysis Toolkit (COMBAT) Demonstrating Capabilities through Practical Examples

by Dylan M Anstine, Chi-Chin Wu, James P Larentzos, and John K Brennan

2020: nAl with coating

PennState Eberly College of Science

Ben Evangelisti
Penn State Univ.



Initial Al_2O_3 slab

CO gas added

Carbon-coated surface

[Evangelisti, *et al.* ARL Tech Report (in preparation)]

CONCLUSIONS

Accomplishments

- Results show potential of energetic nAl via atmospheric plasma surface modifications
- First step plasma treatment with He or Ar plasma leads to 40+% decrease in the oxide shell thickness
- The resultant plasma-thinned and roughened nAl surface leads to increased AlH content of Al@AlH in subsequent wet chemistry mixing
- Second step plasma treatment with H/CO leads to energetic Al@C with faster Al oxidation confirmed by TGA/DSC
- Al@AlH samples show reproducible enhanced lab-scale energetic performance
- Preliminary MD simulation results are consistent with experimental findings

Challenges

Plasma engineering / processing is a COMPLEX science

- Improve reactor design for more uniform plasma treatment on all nAl particles
- Study arcing effects on Al_2O_3 phase transformation & carbon coating
- Measure real time plasma properties to discern active species leading to oxide shell thickness decrease and subsequent energetic coating (AlH or carbon-containing deposits)
- Advanced material characterization is critical but time consuming
- Scale up & technology transition

ACKNOLEDGMENT

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- US Department of Defense, Office of the Under Secretary for the Defense (OUSD) for Applied Research for the Advancement of Science & Technology Priorities Program (ARAP)
- DoD High Performance Computing Internship Program (2019 & 2020)
- ARL Director's Research Award (DIRA) under the External Collaboration Initiative (ECI) – DEC18-WM-009 "Plasma Tailored Smart Surface Aluminum Nanoparticles"

Collaboration:

- Wu, CNM 61797 Proposal "In-situ Nanoscale Structural Analysis of Nanoparticles via Advanced Microscopy"
- ARL-Argonne User Facility Collaboration Agreement
- ARL-TTU CRADA (in process)

QUESTIONS?

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BACKUP SLIDES

23

ARL FACILITIES

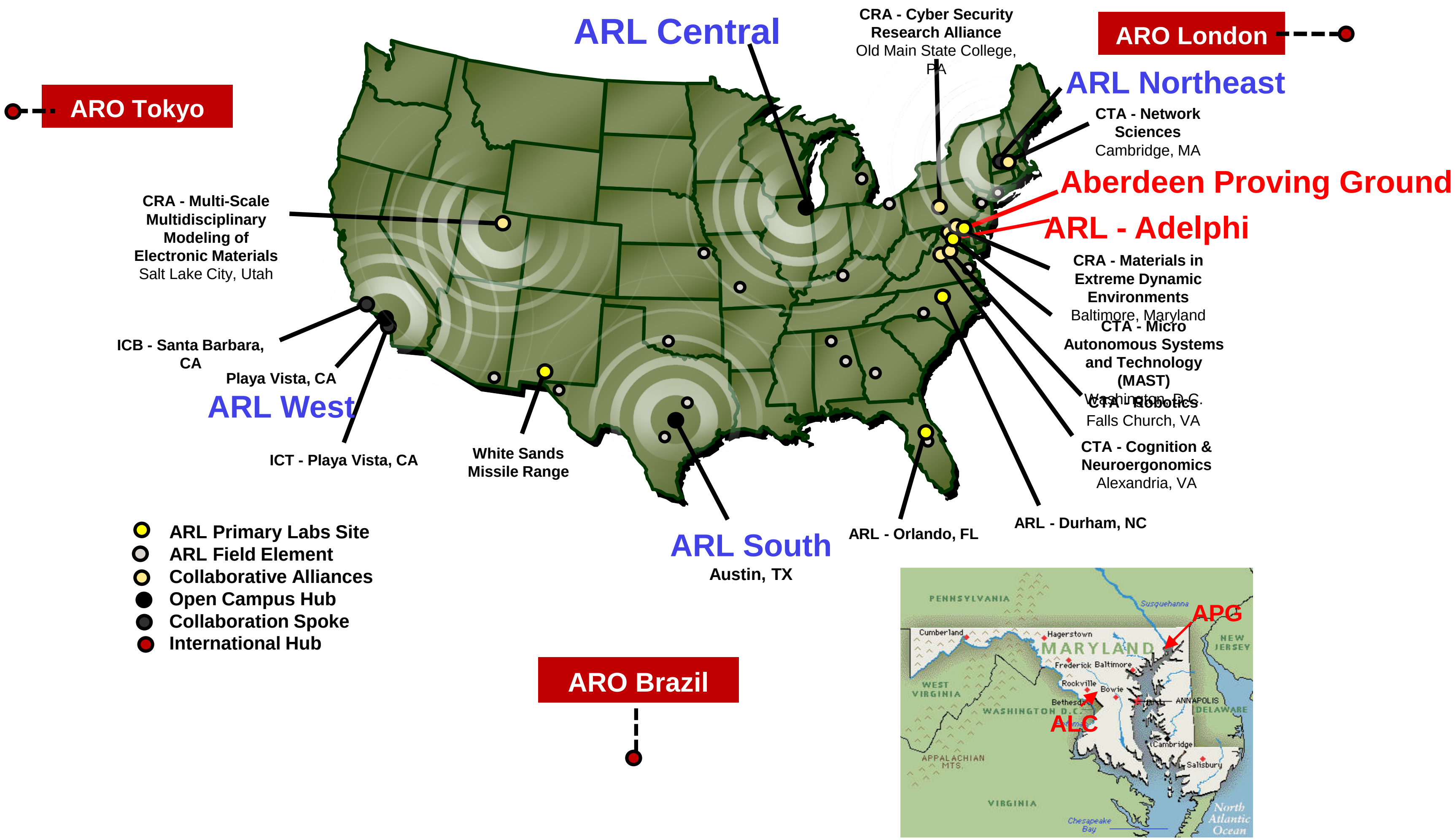
ARL-Adelphi, MD

- Headquarter
- Sensors and Electron Devices
- Computational and Information Sciences

ARL-APG, MD

- Weapons and Materials Research
- Human Research and Engineering
- Vehicle Technology
- Computational and Information Sciences

ARL HUBS



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ARL Northeast
CTA - Network Sciences
Cambridge, MA
Aberdeen Proving Ground
ARL - Adelphi
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Salt Lake City, Utah
CRA - Materials in Extreme Dynamic Environments
Baltimore, Maryland
CTA - Micro Autonomous Systems and Technology (MAST)
Washington, D.C.
CTA - Robotics
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ICT - Playa Vista, CA
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