Harnessing Plasma Experiments with Quantum Calculation for Low-Cost Hydrogen Production

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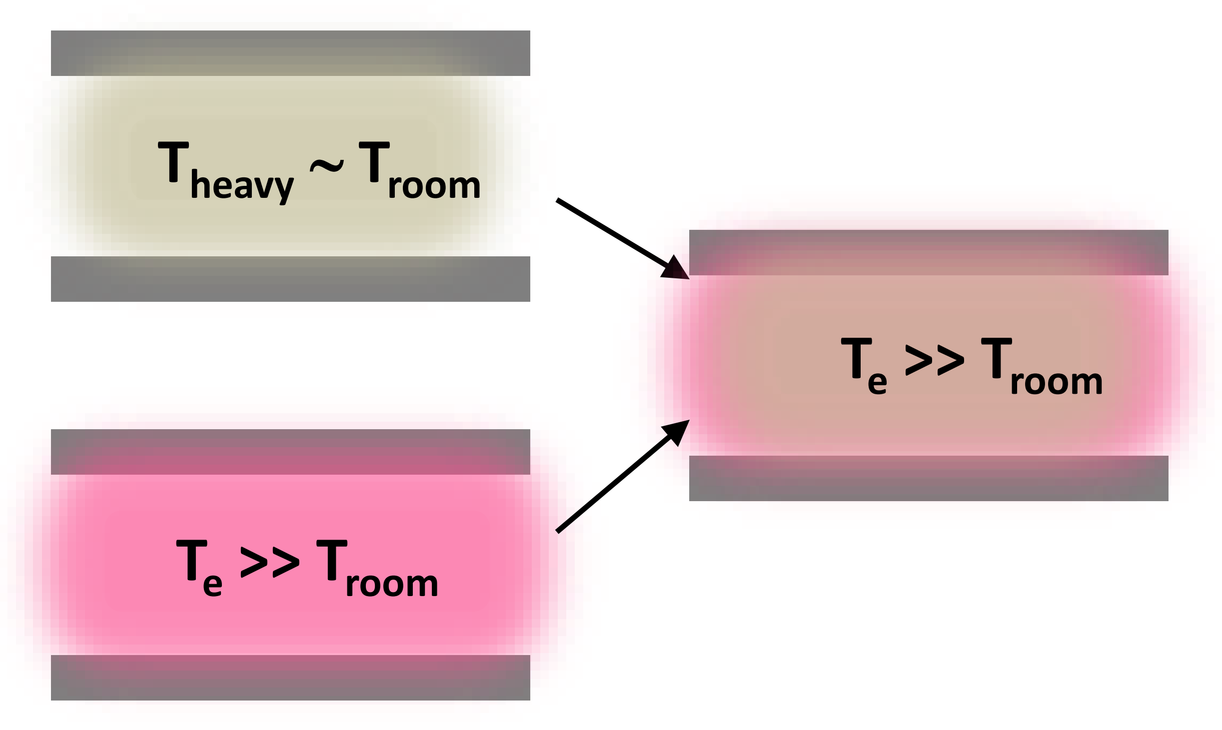
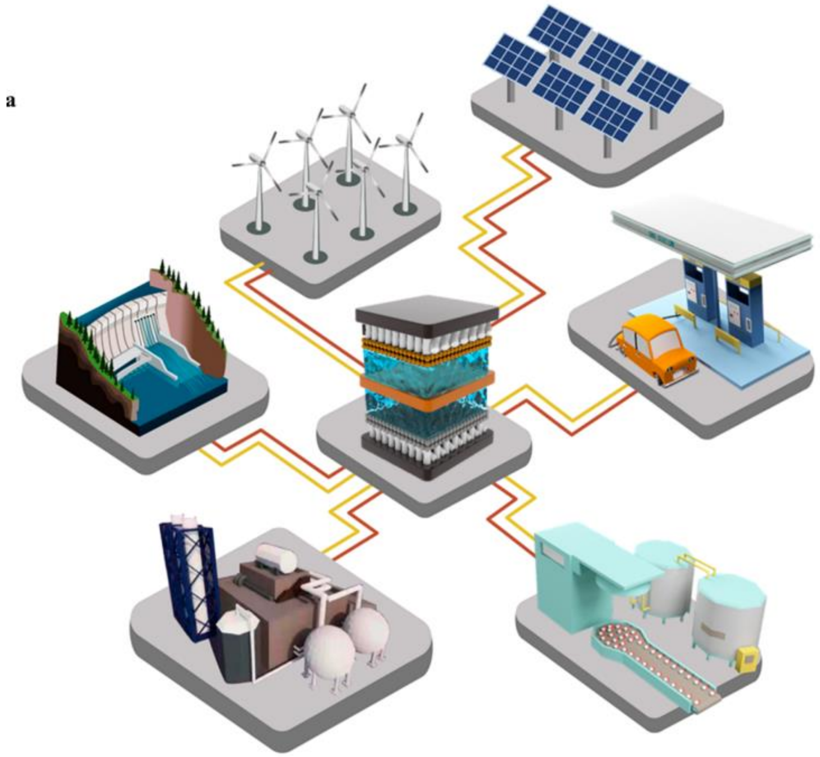
DOE NETL PI meeting – April 2023

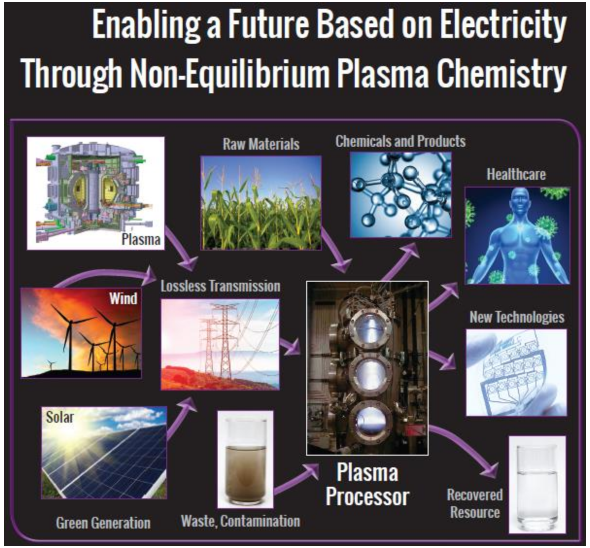
Low temperature non-equilibrium (non-thermal) plasmas



- High electric fields
- Low pressure and/or pulsing

The societal need





Kushner et al. – NSF LTP Workshop Aug 2016

https://arxiv.org/ftp/arxiv/papers/1911/1911.07076.pdf

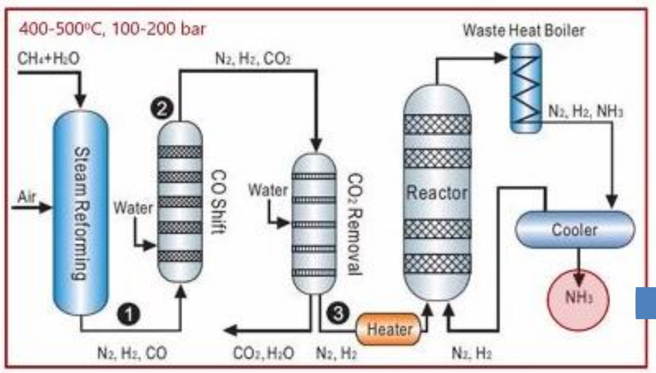
Xia, R., S. Overa, and F. Jiao, *Emerging Electrochemical Processes to Decarbonize the Chemical Industry. JACS Au, 2022.* ***2(5): p. 1054-1070***

Examples – the need for ammonia

How do we make ammonia today? Steam reforming + Haber-Bosch

Natural gas

Air



NH_3
CO_2

Energy

~2 tons CO_2/ton of NH_3

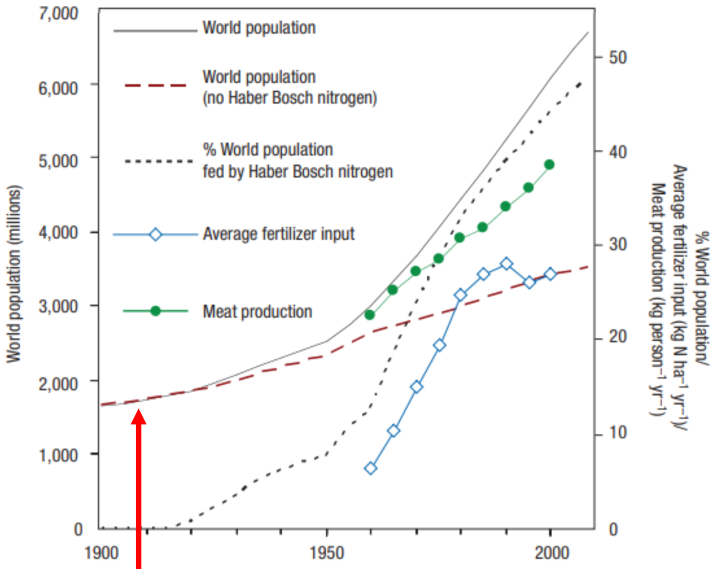
35 GJ/ton$_{NH3}$ ≈ 100 grams NH_3/kWh ≈ 6 eV/NH_3 molecule (12 eV/N_2 molecule)

~250 million tons of ammonia produced via HB per year (as of 2016)

Rouwenhorst, K.H.R., Y. Engelmann, K. van 't Veer, R.S. Postma, A. Bogaerts, and L. Lefferts, *Plasma-driven catalysis: green ammonia synthesis with intermittent electricity.* Green Chemistry, 2020. **22**(19): p. 6258-6287.

About the Haber-Bosch process

- Nitrogen fixation via heterogeneous chemistry
- Ammonia is the feedstock for fertilizer production
- Patented in 1908

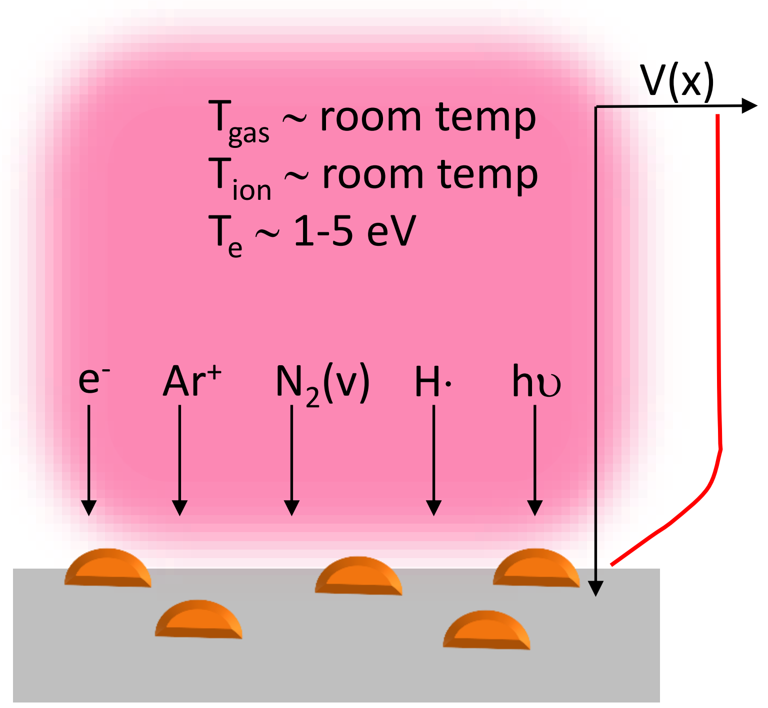


Can we meet demand in a sustainable way?

Erisman, J.W., M.A. Sutton, J. Galloway, Z. Klimont, and W. Winiwarter, *How a century of ammonia synthesis changed the world.* Nature Geoscience, 2008. **1**(10): p. 636-639.

About plasma catalysis

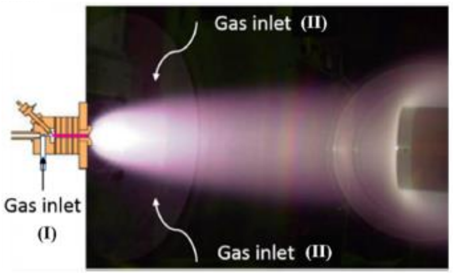
(Non-thermal) activation of heterogeneous chemistry by contact with a (non-thermal) plasma



Complex, difficult to model, difficult to probe experimentally

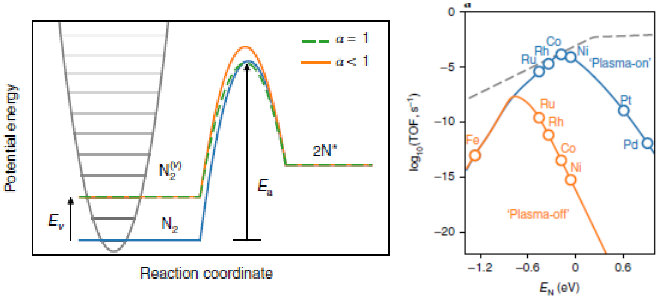
Plasma catalysis for ammonia synthesis – current status

- Several demonstrations of N_2 fixation at room temperature
- Very wide range of process parameters
- <u>Lack of clarity on the main activation pathway</u>



J. H. v. Helden et al., J. Appl. Phys. 101, 043305 (2007).

NH_3 formation of atomic nitrogen recombination at inner walls

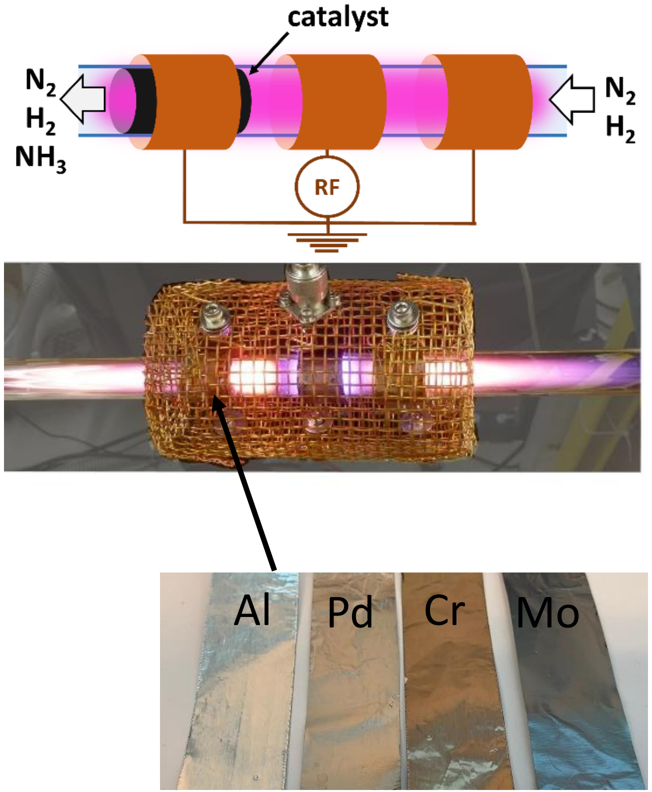


Mehta, P et al.. Nature Catalysis, 2018. **1**(4): p. 269-275

Reduced activation energy for NH_3 formation because of plasma-induced N_2 vibrational excitation

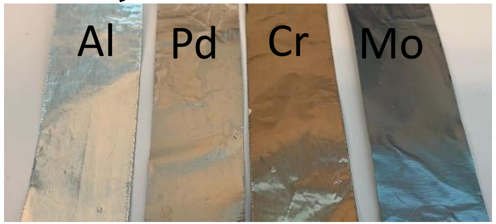
Our approach

Characterization of low-pressure RF plasma / Born-Oppenheimer Molecular Dynamics (BOMD) simulation

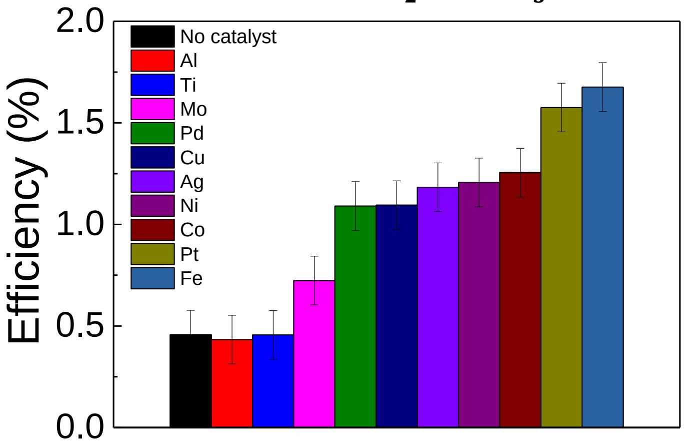


- 1 Torr, flow-through, 1:3 N_2:H_2
- Spatially and temporally uniform
- Inner wall lined with different metals

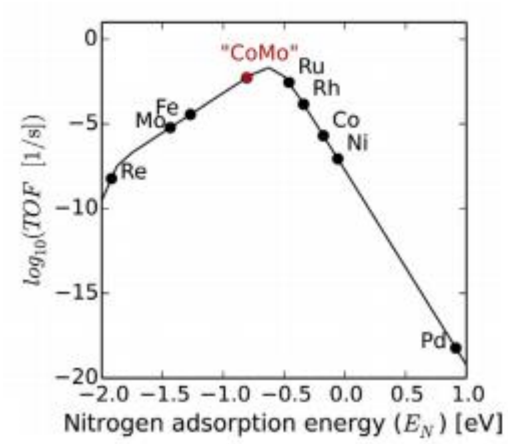
Reactor-level ammonia yield



$$\eta = \frac{P_{NH_3}}{2 \cdot P_{N_2} + P_{NH_3}}$$



Heterogeneous catalysis – basic concepts

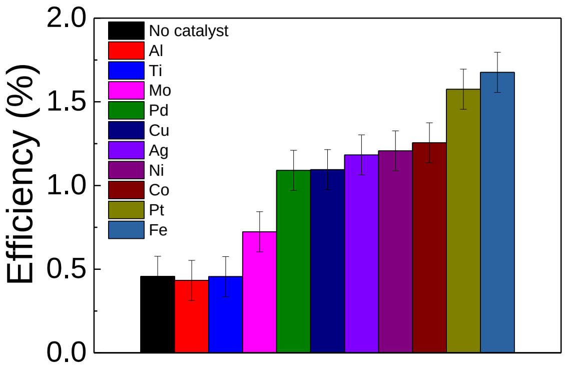


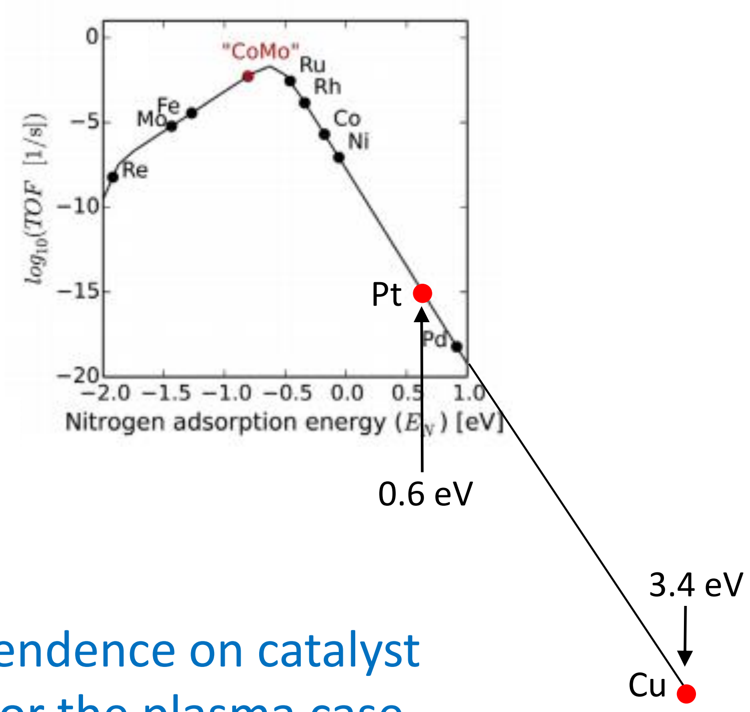
- $E_N = E_{N2\text{-metal complex}} - E_{metal} - E_{N2}$
- Activation energy for N_2 dissociation is proportional to E_N (BEP relations)
- Low E_N: N_2 dissociates but products do not desorb
- High E_N: N_2 does not interact with surface
- Strong dependence of reaction rate on E_N

Medford, A.J., A. Vojvodic, J.S. Hummelshøj, J. Voss, F. Abild-Pedersen, F. Studt, T. Bligaard, A. Nilsson, and J.K. Nørskov, *From the Sabatier principle to a predictive theory of transition-metal heterogeneous catalysis.* Journal of Catalysis, 2015. **328**: p. 36-42.

Evans, M.G. and M. Polanyi, *Inertia and driving force of chemical reactions.* Transactions of the Faraday Society, 1938. **34**(0): p. 11-24.

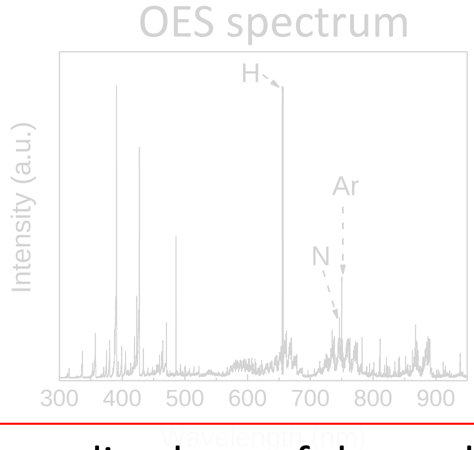
Plasma-drive catalysis



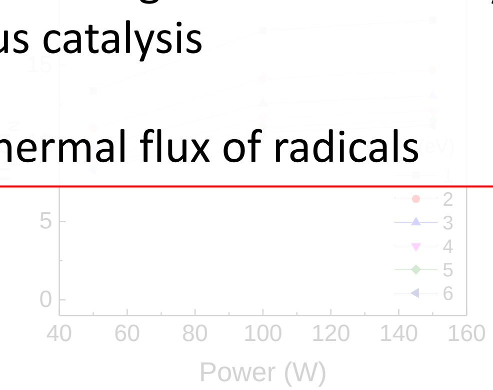


Weak dependence on catalyst material for the plasma case

Plasma characterization



- Actinometry used to obtain the density of atomic N and H species
- Atomic H density exceeds N density
- $n_H = 4\times10^{14}$ cm^{-3}; $n_N = 4\times10^{13}$ cm^{-3}



The process does not follow the same scaling laws of thermally-driven heterogeneous catalysis

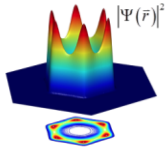
Catalyst is exposed to a super-thermal flux of radicals

E. Tatarova et al., Plasma Sources Science and Technology **14**, 19 (2004).

Modelling of plasma-surface interaction – BOMD

- In collaboration with the group of B. Wong at UCR
  https://www.bmwong-group.com/

Prof. Bryan M. Wong
Nanoscale & Mesoscale Energy Materials Group



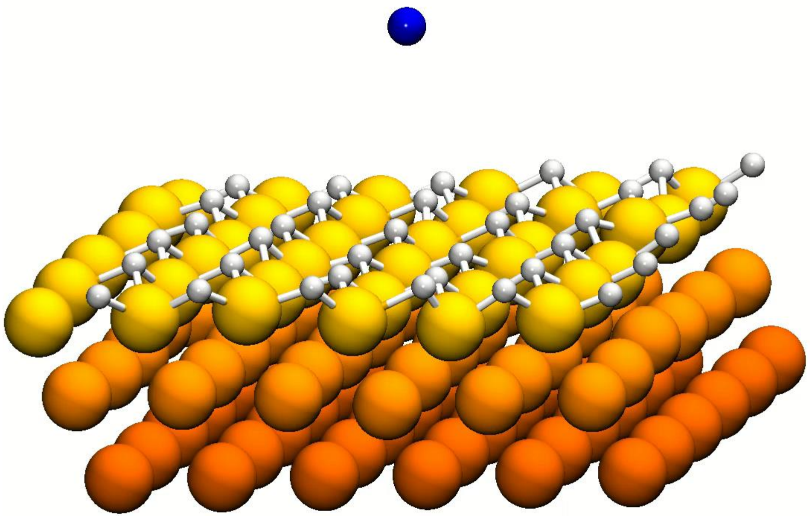
- Born Oppenheimer Molecular Dynamics (BOMD) provides direct, dynamical, and unbiased approach for predicting reaction mechanisms on surfaces

- Potential energies are computed in an ab-initio manner; BOMD is superior to classical molecular dynamics (MD), particularly for radical species, whish are probed in plasma processes

- **Can also handle temperature effects that static DFT does not include**

Modelling of plasma-surface interaction – case 1: Cu

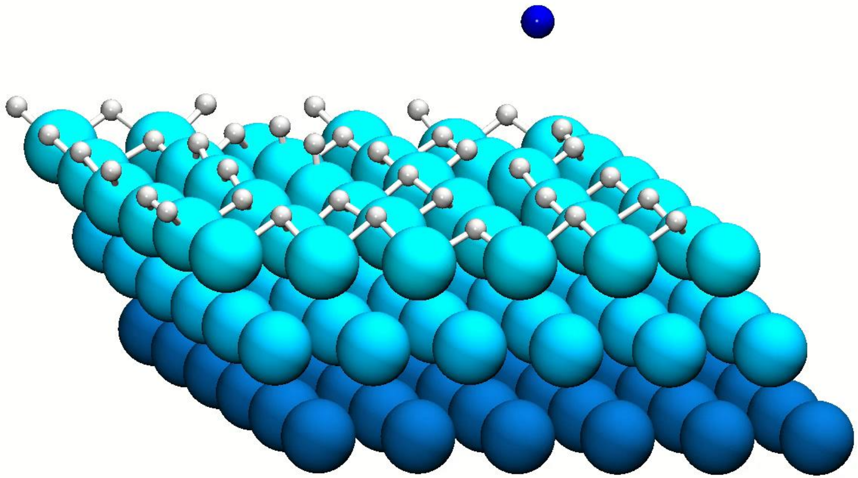
We consider the case of atomic nitrogen impinging on a H-terminated surface



- Atomic N on Cu (111) – 6x6 cell, 3 layers
- Duration = 2 ps
- **Rapid NH_3 formation via Eley-Rideal mechanism**

Modelling of plasma-surface interaction – case 2: Pt

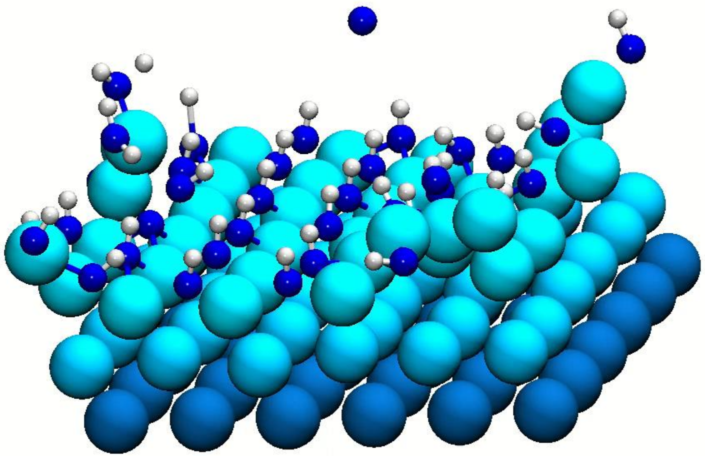
We consider the case of atomic nitrogen impinging on a H-terminated surface



- Atomic N on Pt (111) – 6x6 cell, 3 layers
- Duration = 2 ps
- **Adsorption of N onto Pt**

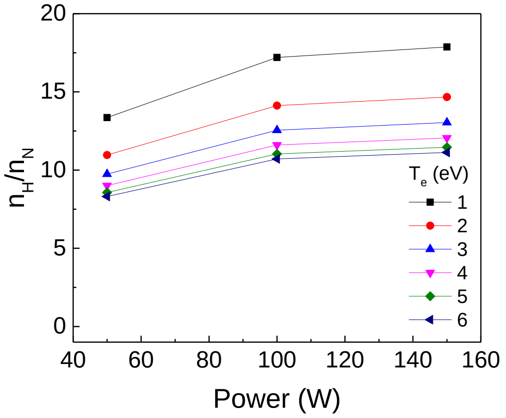
Modelling of plasma-surface interaction – case 2: Pt

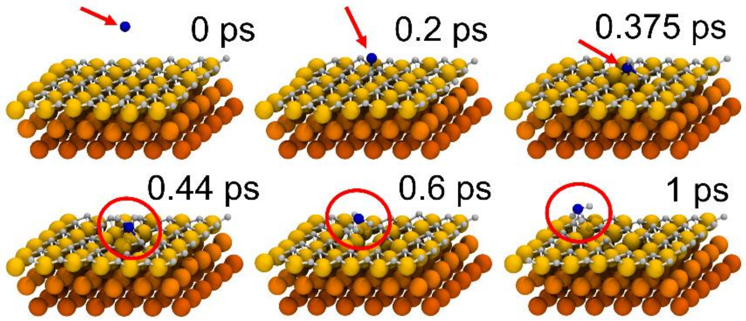
Since H-flux largely exceeds the N-flux, we consider the case of N impinging on a NH-terminated Pt surface



- Atomic N on Pt (111) – 6x6 cell, 3 layers
- Duration = 2 ps
- **Rapid NH_3 formation via Eley-Rideal mechanism**

Summary

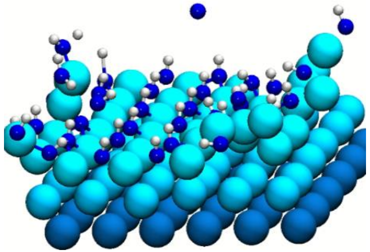




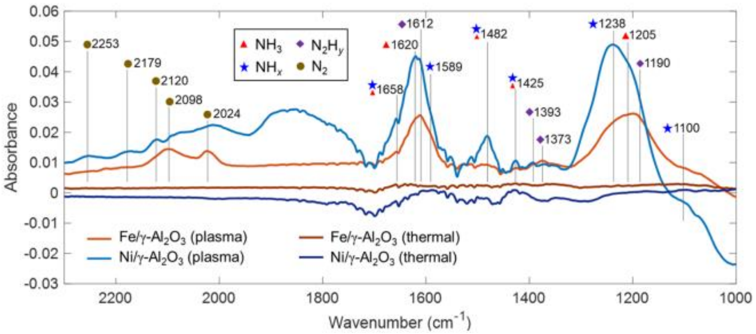
- n_H flux >> n_N flux
- Different surface termination but ultimately same mechanism (direct abstraction)
- Fast surface kinetics (<2 ps)
- Consistent with a mass-transport limited reaction pathway, in agreement with the weak material dependence

S. S. R. K. C. Yamijala, G. Nava, Z. A. Ali, D. Beretta, B. M. Wong, and L. Mangolini, *Harnessing Plasma Environments for Ammonia Catalysis: Mechanistic Insights from Experiments and Large-Scale Ab Initio Molecular Dynamics*, The Journal of Physical Chemistry Letters **11**, 10469 (2020).

Summary

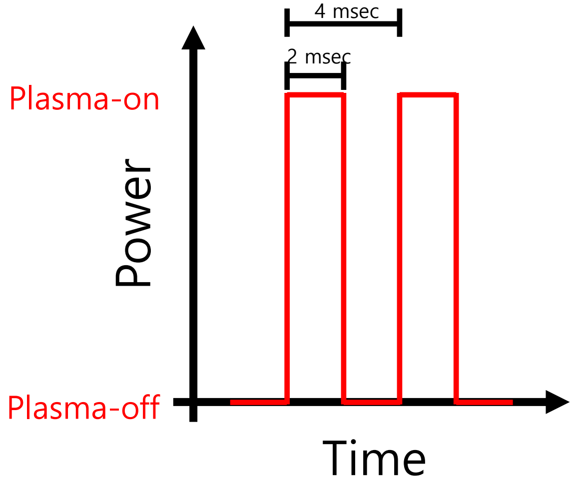


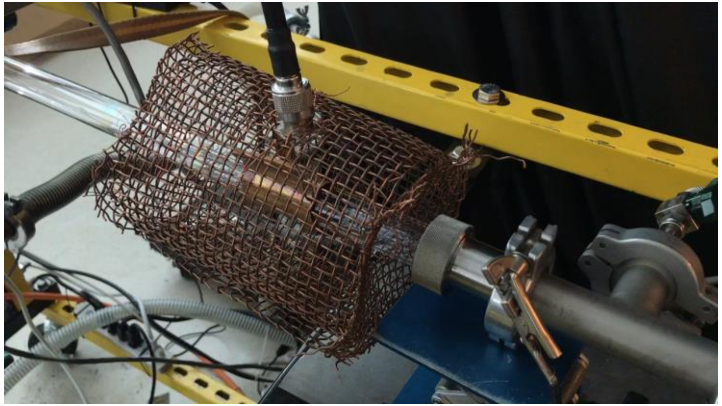
NH$_x$ termination of metal surfaces under plasma exposure has been confirmed experimentally



Winter, L.R., B. Ashford, J. Hong, A.B. Murphy, and J.G. Chen, *Identifying Surface Reaction Intermediates in Plasma Catalytic Ammonia Synthesis.* ACS Catalysis, 2020. **10**(24): p. 14763-14774.

About the process energy cost

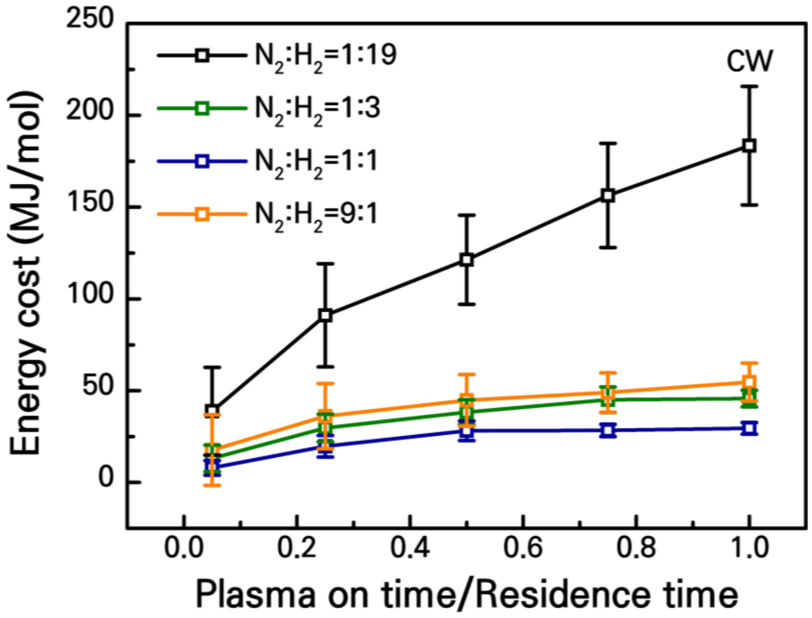


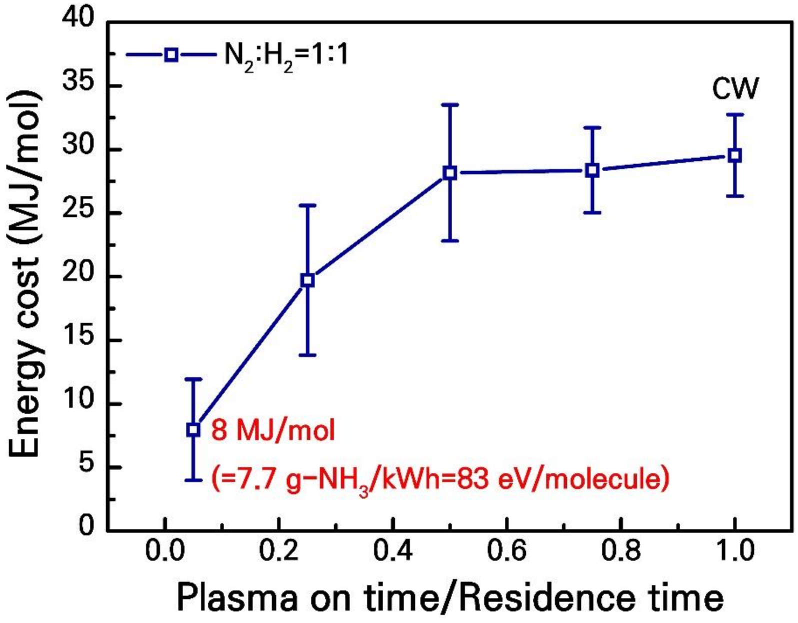


How do we lower the energy cost of plasma-driven processes?

Energy cost and pulsed operation

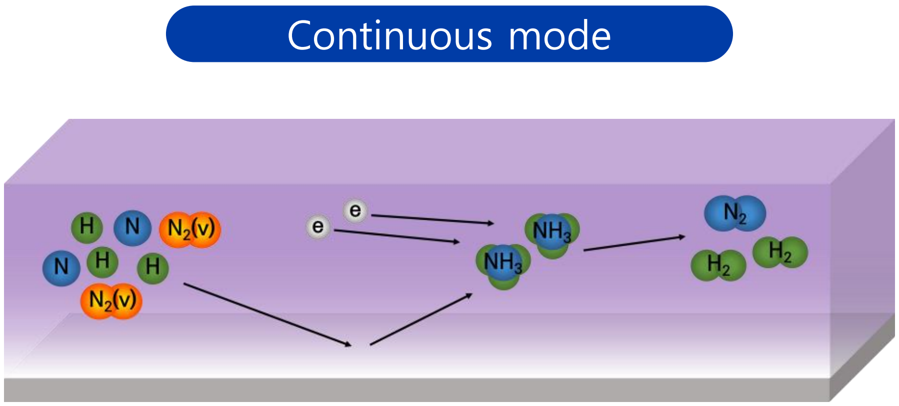
One pulse per residence time

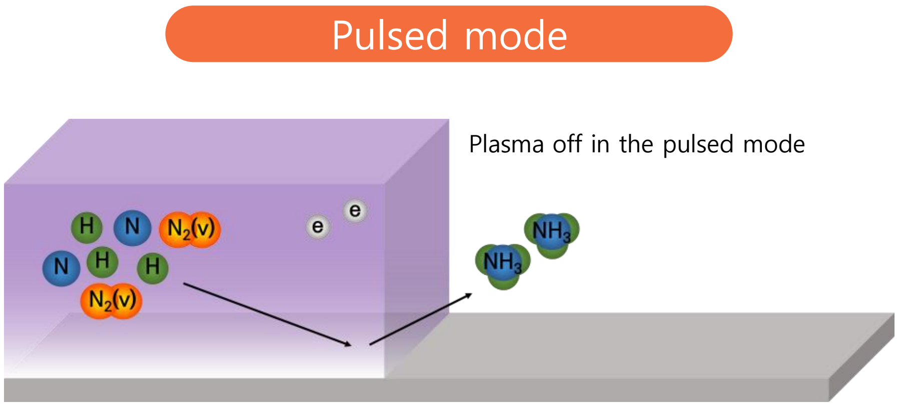




Minimum energy cost at τ_{pulse} = 2 msec

Energy cost and pulsed operation

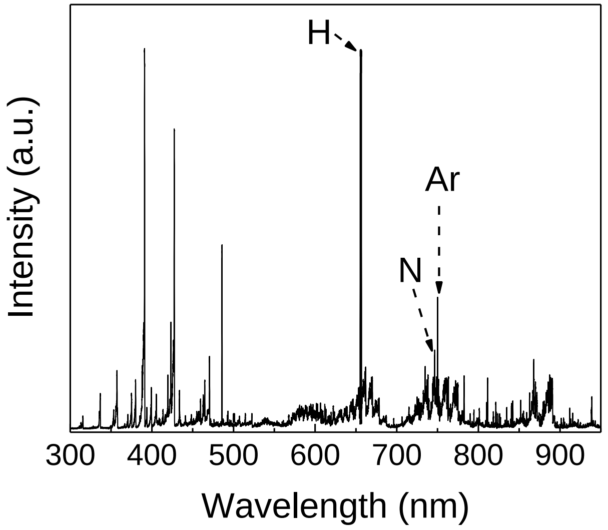


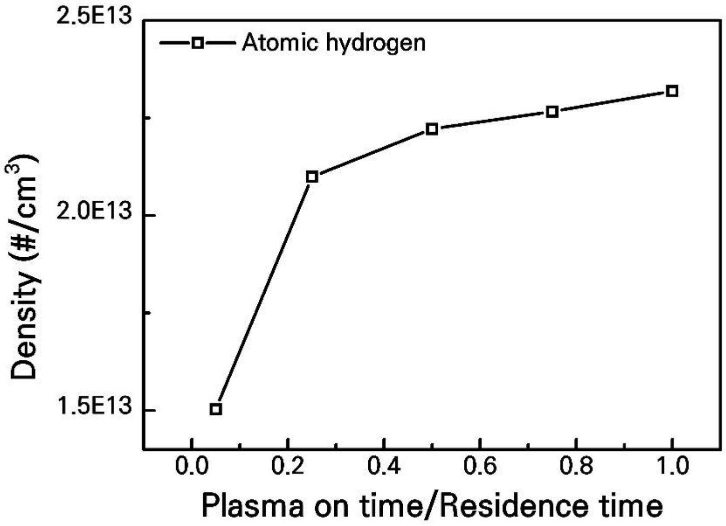


	N_2	H_2	NH_3
Dissociation Energy (eV)	9.8	4.5	3.7

- The plasma environment also dissociates the desired reaction product
- The key is to extinguish the plasma before NH_3 diffusion from the reactor wall
- Diffusion time ~1 msec

Energy cost and pulsed operation



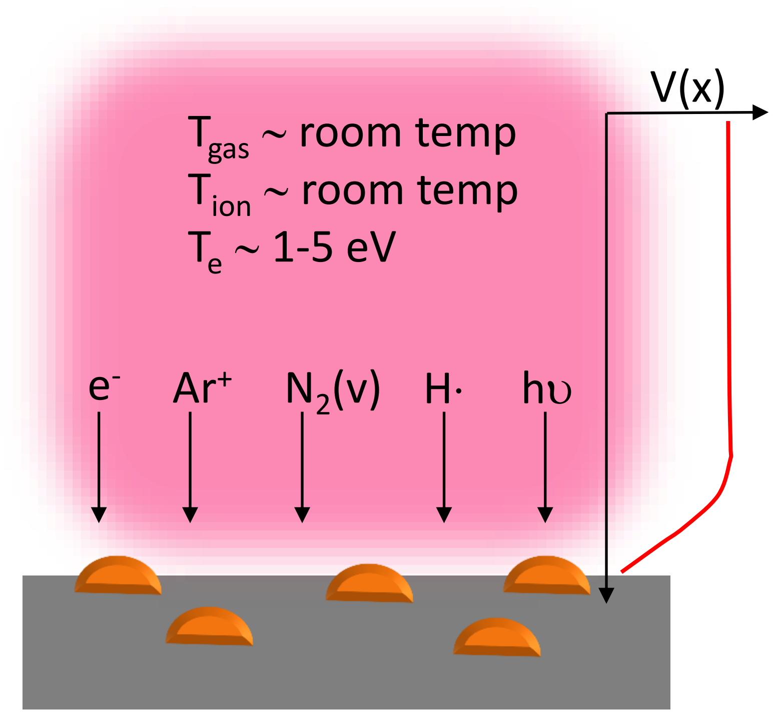


The drop in atomic hydrogen density is consistent with the fact that there is less ammonia in the plasma volume

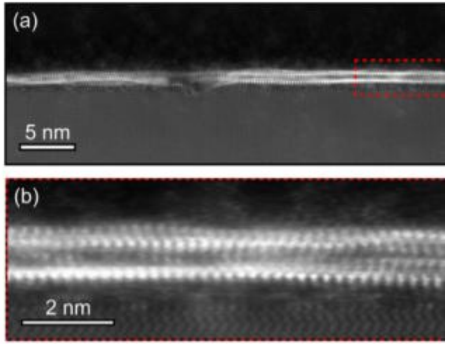
Kim, M., S. Biswas, G. Nava, B.M. Wong, and L. Mangolini, *Reduced Energy Cost of Ammonia Synthesis Via RF Plasma Pulsing. ACS Sustainable Chemistry & Engineering, 2022. 10(46): p. 15135-15147.*

The plasma-surface interface

- The localized release of energy at plasma-exposed surfaces, a.k.a. “plasma heating”, is poorly characterized.
- It is crucial for many plasma-related applications.



Plasma heating: implications

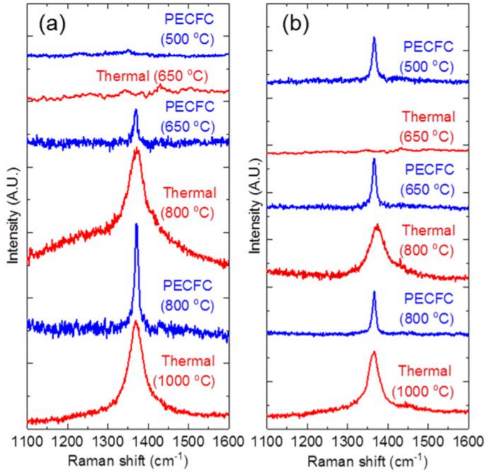


PECVD of MoS_2 at 500°C

Beaudette, C. A. et al., ACS Omega **5**(34): 21853-21861, (2020)

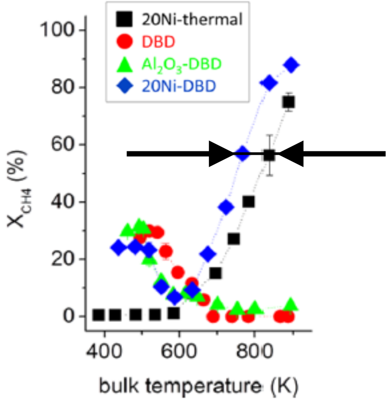
Ar

Ar + H_2

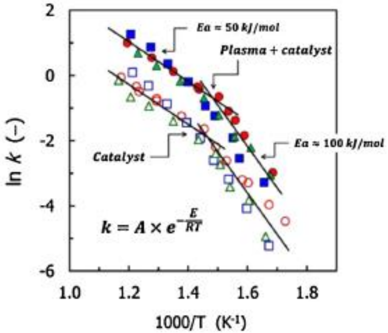


Plasma-assisted conversion of chemical precursor into high-quality hBN

Liu, T. et al. ACS Applied Materials & Interfaces **10**(50): 43936-43945 (2018).



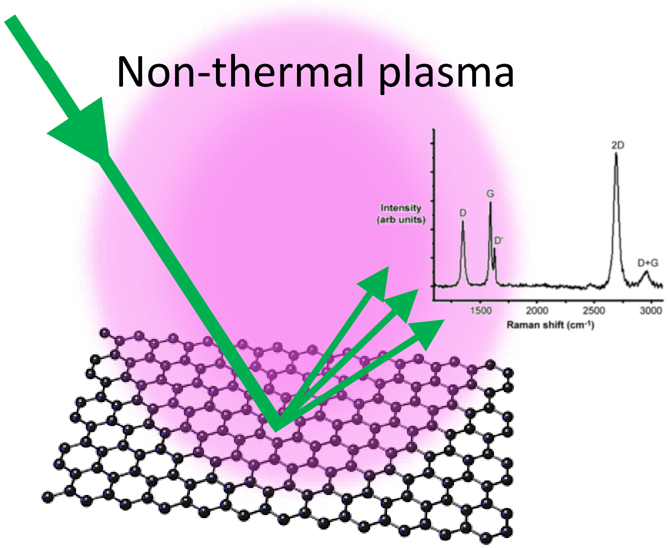
J. Kim et al., ACS Energy Letters **1**, 94 (2016).

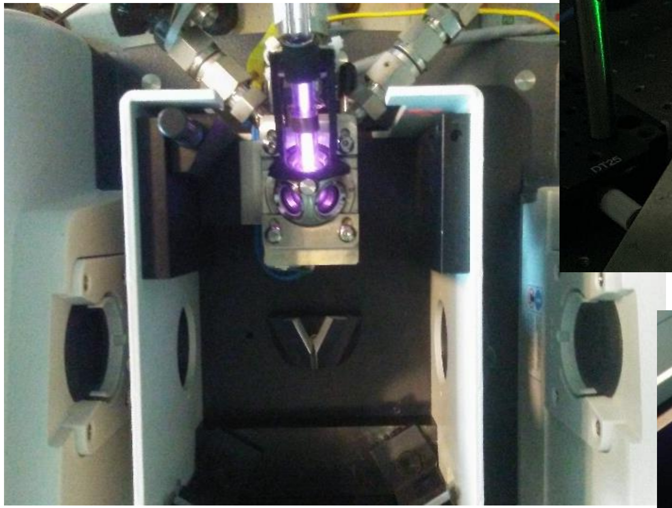


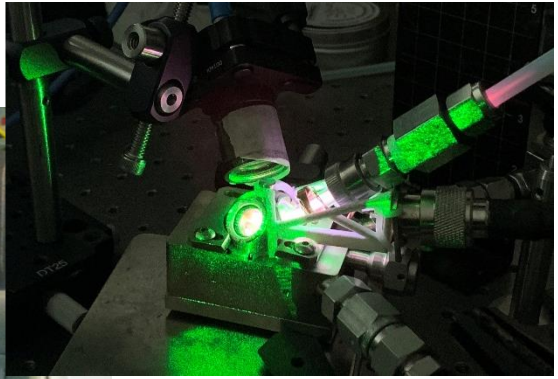
T. Nozaki and K. Okazaki, Catal. Today **211**, 29 (2013).

How can we quantitatively probe “plasma heating”?

Graphene as a surface-specific temperature probe

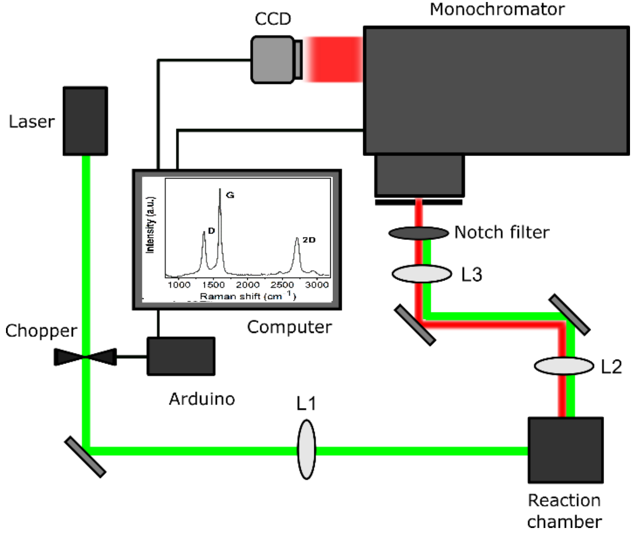


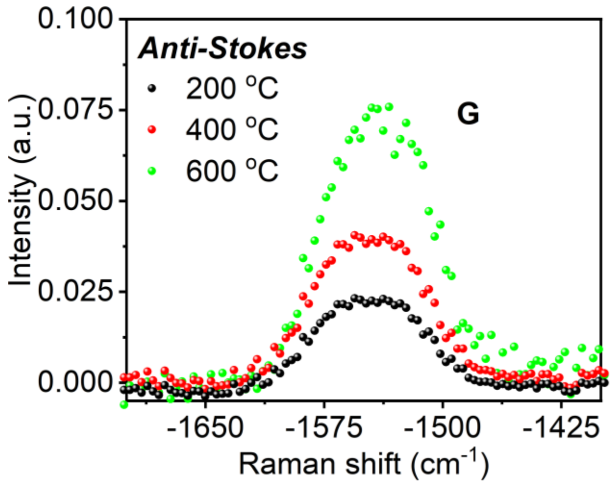




Substrate is temperature-controlled
(up to 900°C)

Surface temperature measurement

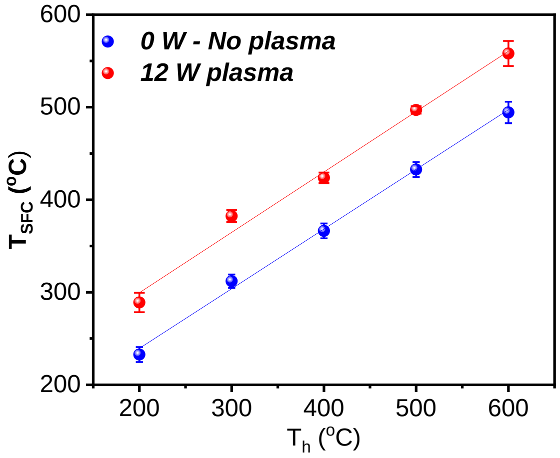




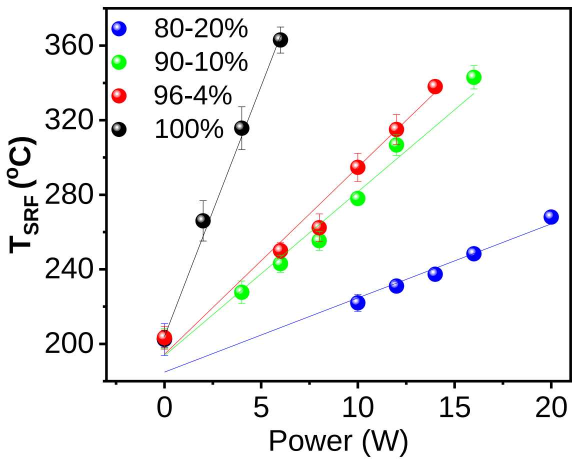
Lock-in measurement to remove plasma emission background

$$\frac{I_s}{I_{as}} = \left(\frac{\lambda_s}{\lambda_{as}}\right)^4 e^{-hv/kT}$$

Surface temperature measurement



Constant plasma power
Varying substrate temperature

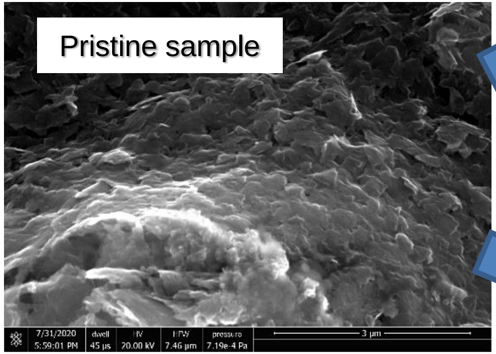


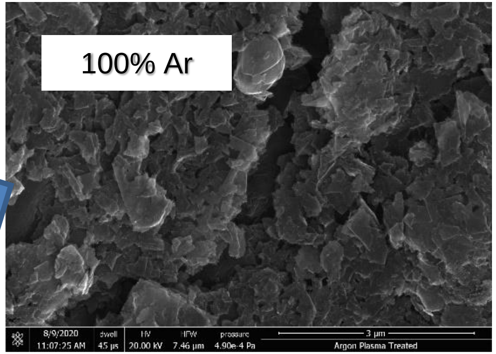
Constant substrate temperature (200°C)
Varying plasma power and composition (Ar-H_2)

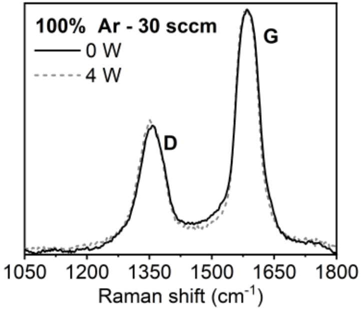
Substantial heating even at modest plasma power

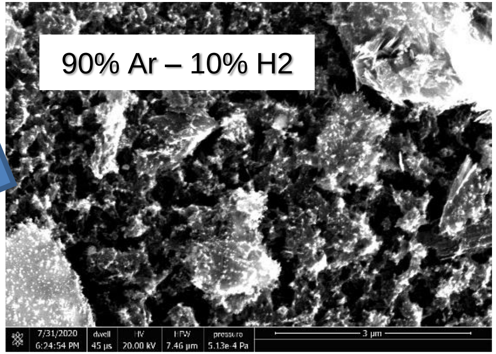
C. Berrospe-Rodriguez, J. Schwan, G. Nava, F. Kargar, A. A. Balandin, and L. Mangolini, *Interaction Between a Low-Temperature Plasma and Graphene: An in situ Raman Thermometry Study*, Physical Review Applied **15**, 024018 (2021).

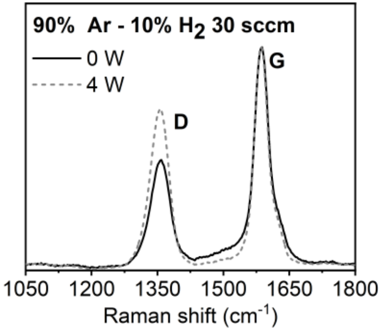
Surface temperature measurement





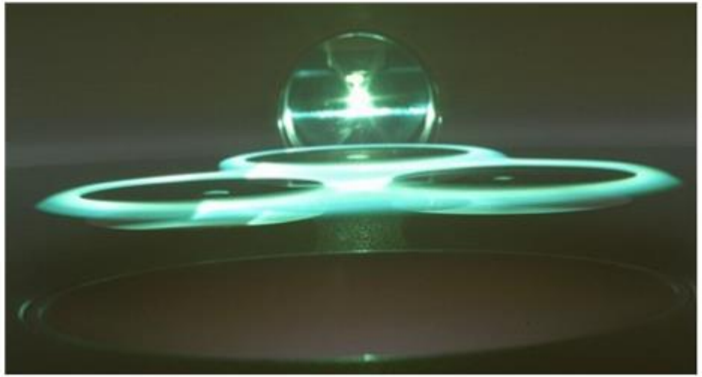






Plasma exposure leads to surface defects

Low-temperature plasmas for nanoparticle synthesis

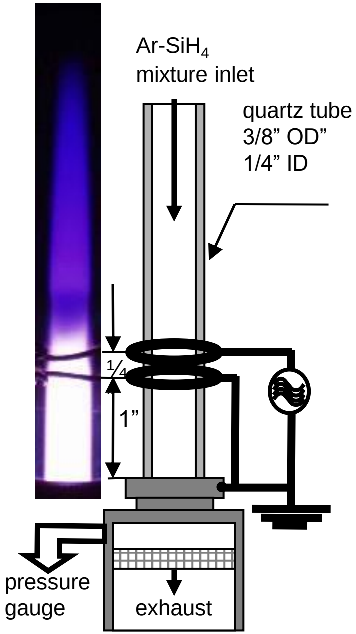


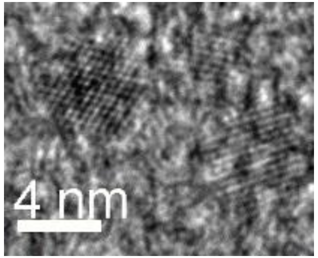
Selwyn et al., Plasma Sources Science and Technology, 3, 340 (1994)

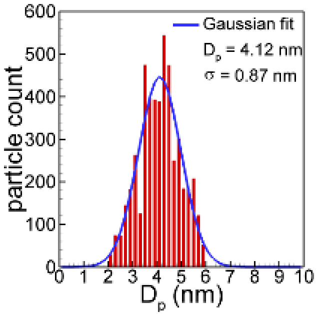
- Intense scattering induced by particles which are nucleated and grown by the plasma
- Early focus: prevent particle formation in plasmas

Particles in plasma: from problem to opportunity

Let’s use plasmas to deliberately produce nanoparticles!





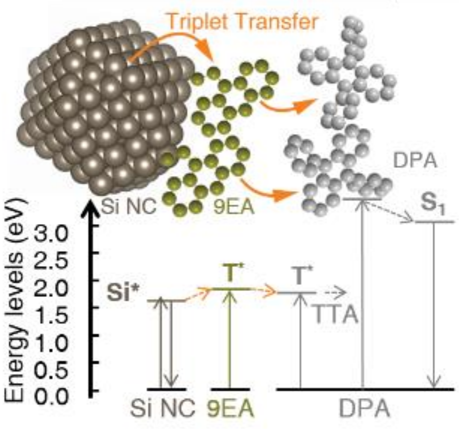


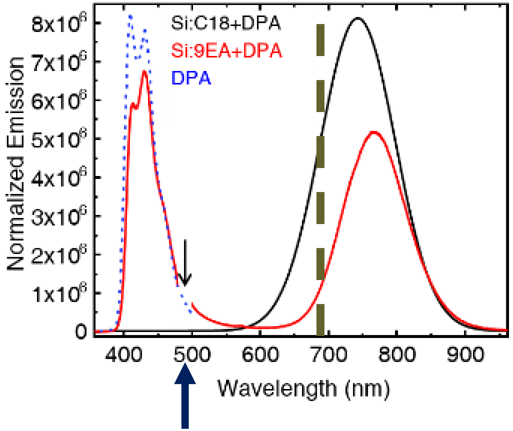
- Continuous precursor-to-particle conversion
- Near 100% silane utilization

Mangolini, L., E. Thimsen, and U. Kortshagen, *High-yield plasma synthesis of luminescent silicon nanocrystals*, Nano Letters, 2005. **5**(4): p. 655-659

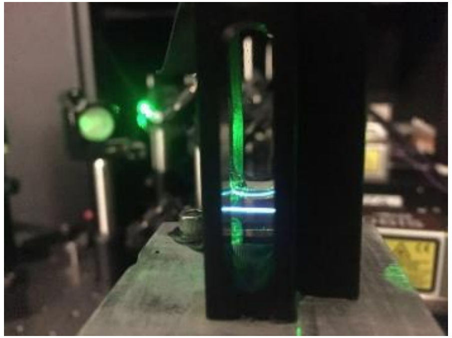
Process and apparatus for forming nanoparticles using radiofrequency plasmas - US7446335B2

Upconversion in SiQDs





excitation

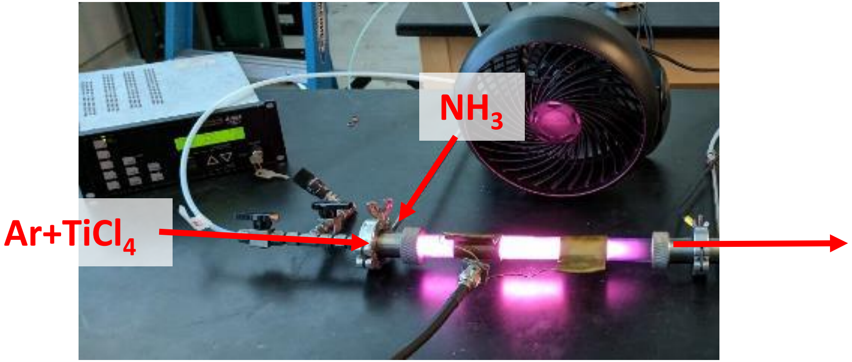


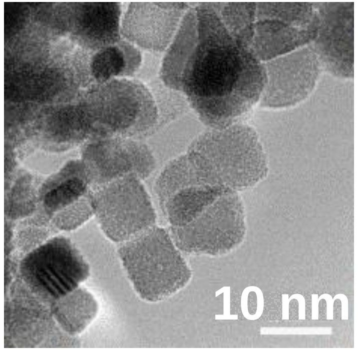
Up-conversion of green-blue (488 nm) to UV (<450 nm)

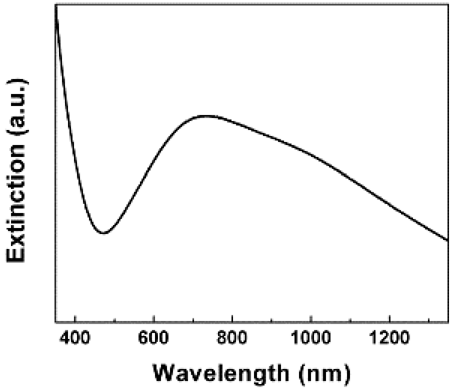
Energy transfer from SiQD to triplet state in 9EA group (~15 nsec), followed by triplet-triplet fusion in DPA

Xia, P., E.K. Raulerson, D. Coleman, C.S. Gerke, L. Mangolini, M.L. Tang, and S.T. Roberts, *Achieving spin-triplet exciton transfer between silicon and molecular acceptors for photon upconversion.* Nature Chemistry, 2020. **12**(2): p. 137-144.

Plasma synthesis of titanium nitride nanoparticles



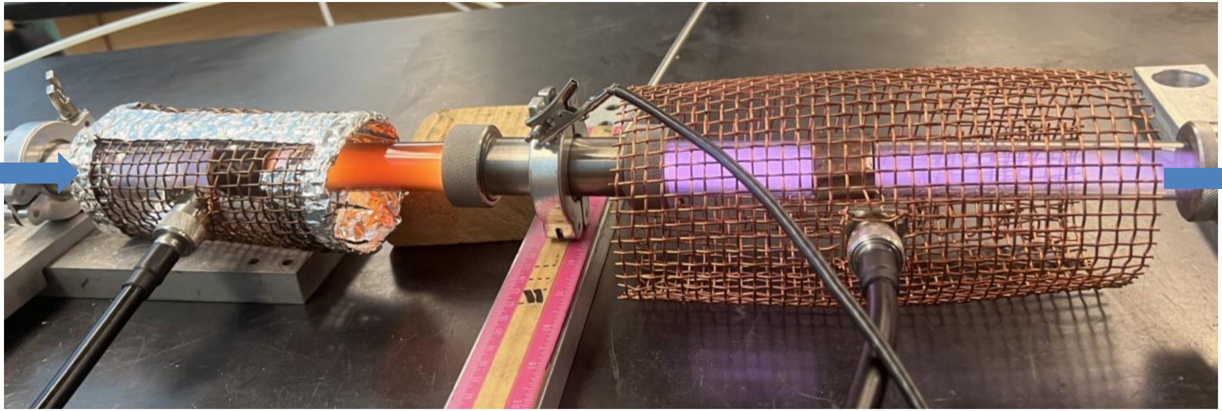




Alvarez Barragan, A., N.V. Ilawe, L. Zhong, B.M. Wong, and L. Mangolini, *A Non-Thermal Plasma Route to Plasmonic TiN Nanoparticles.* The Journal of Physical Chemistry C, 2017. **121**(4): p. 2316-2322.

Nanoparticle nucleation for H_2 gas generation

CH_4



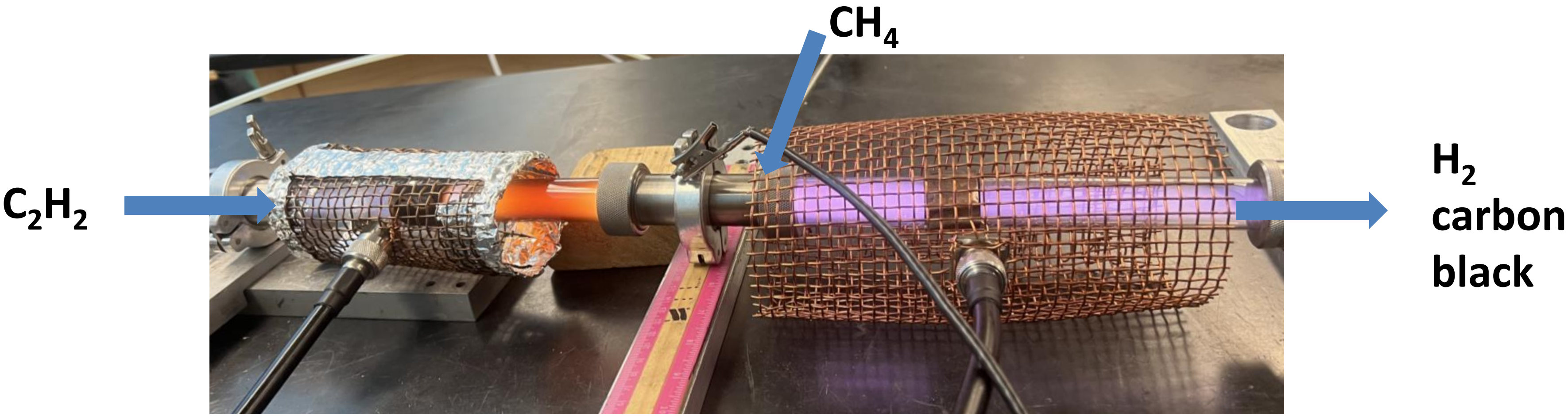
H_2
carbon
black

Can we nucleate and grow carbon particles from a methane plasma?

Can such particles be functionally useful?

Is the process energy efficient?

Nanoparticle nucleation for H_2 gas generation

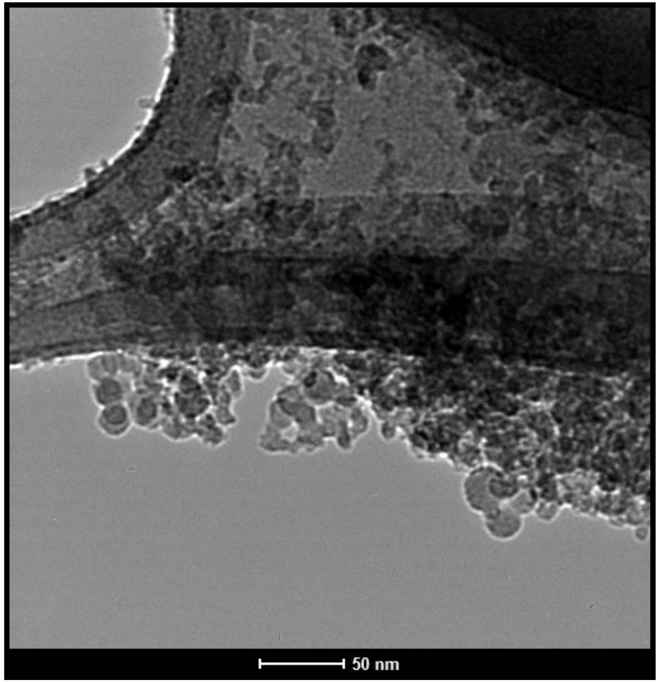


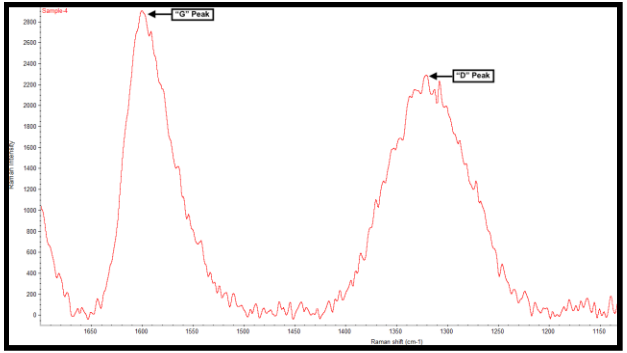
Can we nucleate and grow carbon particles from a methane plasma? **No**

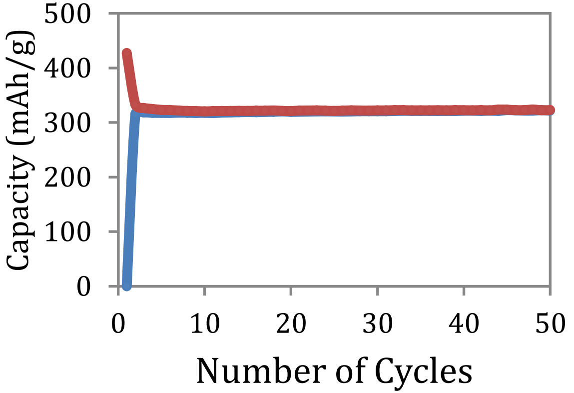
Plasma needs to be pre-seeded

With pre-seeding, CH_4 conversion can be efficient (20%)

Nanoparticle nucleation for H_2 gas generation







Can such particles be functionally useful? **YES**

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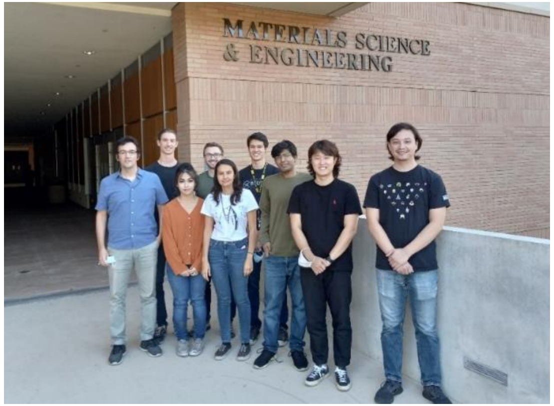

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