Plasma Catalysis

Maria Carreon
South Dakota School of Mines & Technology
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Introduction/Background

Personal Background

- Born 3/25/1984 in Morelia, Mexico.
- BS Chemical Engineering (2007) at Universidad Michoacana (UMSNH), Mexico.
- MS Chemical Engineering (2010) at Universidad Michoacana (UMSNH), Mexico.
- PhD Chemical Engineering at University of Louisville 2015.
- Assistant Professor at the University of Tulsa, Russell School of Chemical Engineering, Fall 2015-Spring 2019.
- Assistant Professor at SDSMT, Chemical & Biological Engineering Department, Summer 2019-Present.

Carreon Lab

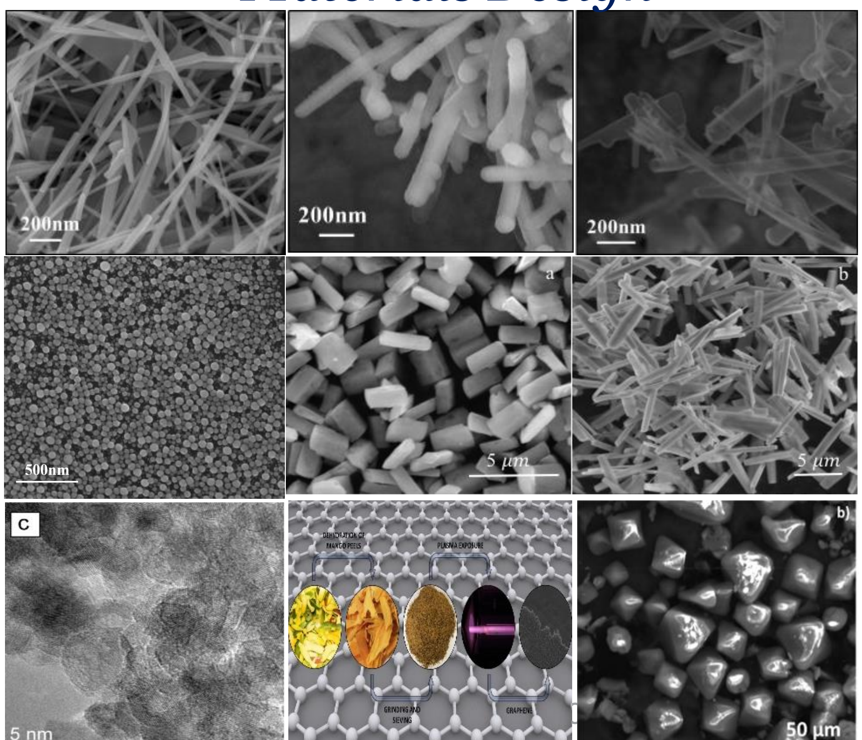
https://mariacarreong.wixsite.com/carreon

Research interests:

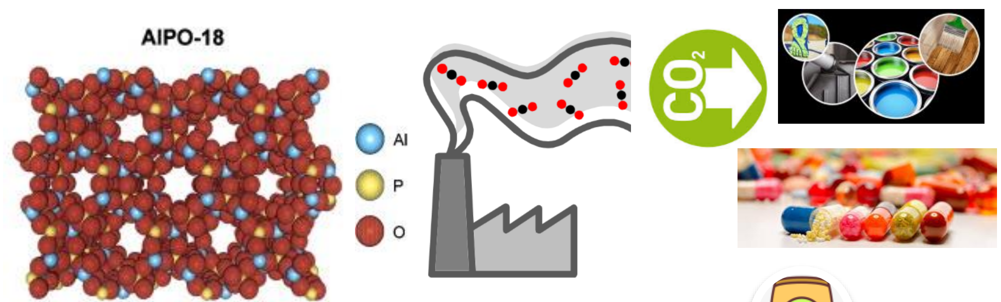
- Rational design of porous materials at different length scales, including Zeolites, Mixed Metal Oxides, Nanowires, Nanotubes, Thin Films, Graphene and MOFs (Metal Organic Frameworks).
- Formation mechanisms of these materials to establish fundamental structure/separation, catalytic and adsorption relationships.

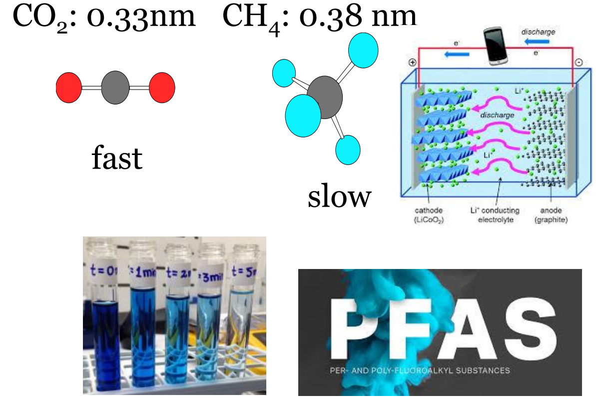
Research Areas: Zeolite Membranes; Rational Design of Heterogeneous Catalysts; CO_2 Conversion to Chemicals; Plasma Catalytic reactions.

Materials Design



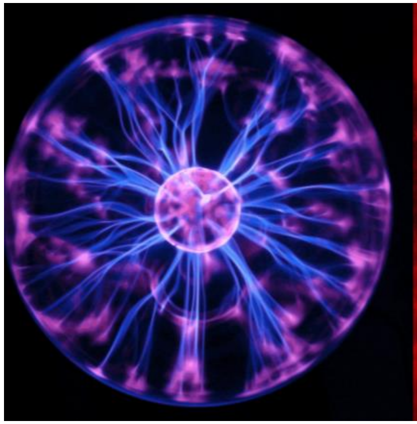
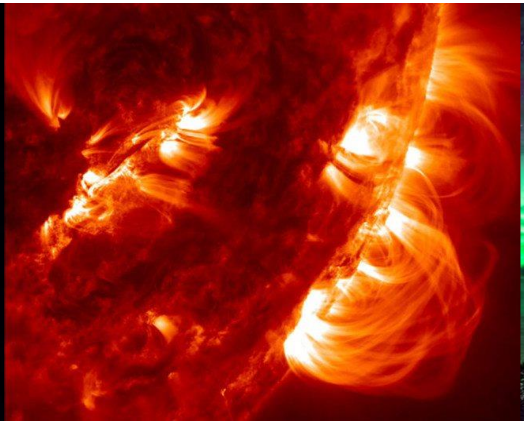
Functional Applications





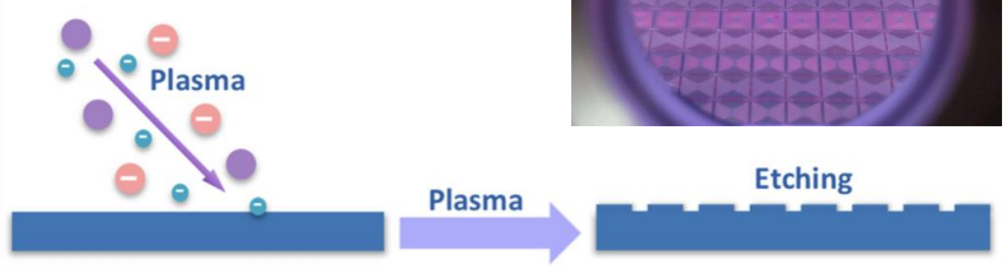
Plasma Definition

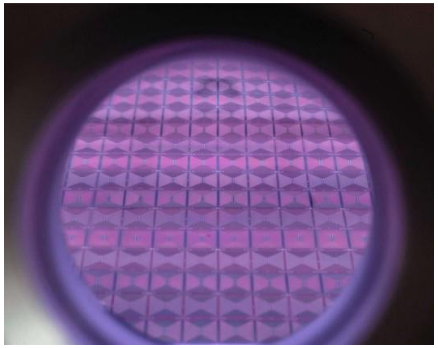
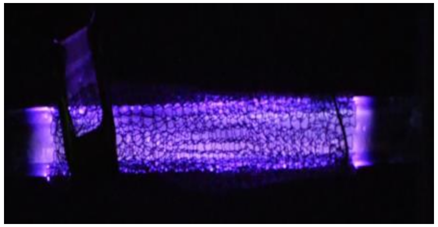
- Plasma is considered as the fourth state of matter.
- Plasma comprise 99.9% of the visible universe.
- Typically, plasma is generated by driving an electrical current through gas.
- Plasma contains electrons, neutrals, and highly excited atomic, molecular, ionic and radical species.
- Two types of Plasma: Thermal and Non-Thermal (NTP)
- In NTP, electrons are usually at very high temperatures because of their smaller mass, whereas ions and background gas are at room temperature (safe to touch).

Non-thermal plasma (NTP)

- Non-thermal plasmas exhibit higher selectivity compared to thermal plasmas.
- Non-thermal plasmas are the most commonly used plasmas for technological applications.
- The electron temperature in NTPs range from 0.01-16 eV. Range extremely suitable for chemical reactions as the bond dissociation and ionization energies of atoms and molecules fall in this regime.
- The challenge: to employ successfully targeted excited species in order to form the desired products. This can be achieved with the help of a catalyst.

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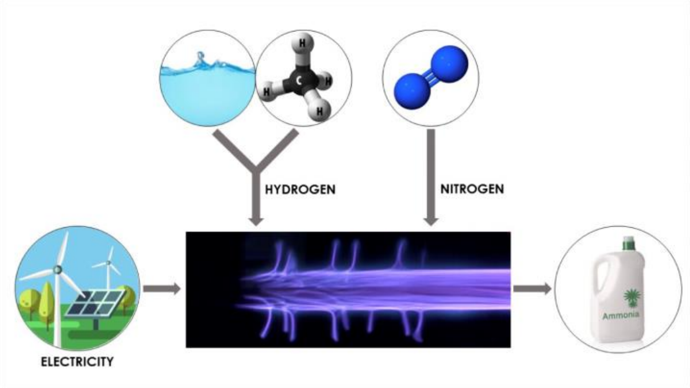
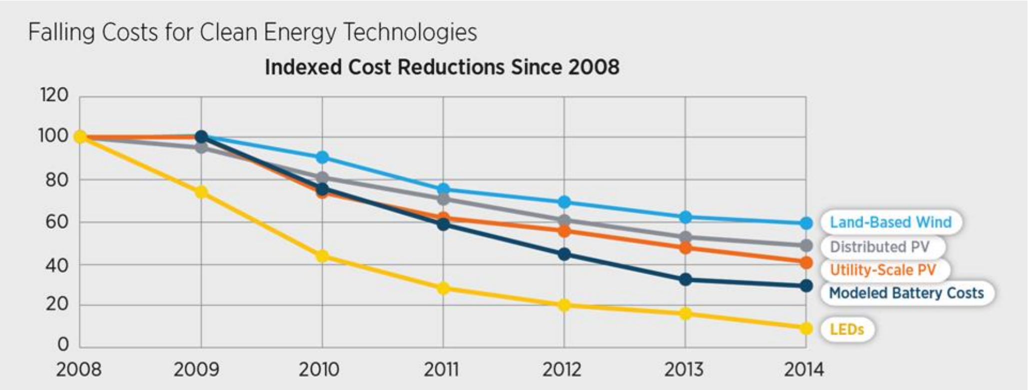
<u>Carreon, Maria L.</u> *"Plasma catalysis: a brief tutorial." Plasma Research Express 1, no. 4 (2019): 043001.*

Non-thermal plasma systems motivation

Plasma reactor/ process offers advantages such as:
(1) simple one step processes,
(2) operated and stopped instantaneously – switch on and off
(3) very fast reactions – resulting in smaller units,
(4) generally non-polluting.

Plasma technology has the potential to provide a convenient route to store renewable electricity in a flexible way and convert it into chemicals thorough highly efficient reactions.





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https://obamawhitehouse.archives.gov/blog/2015/11/13/investments-renewable-energy-are-paying-and-paving-way-ambitious-climate-action

What we have learnt from plasma catalytic ammonia synthesis

- Under plasma environment all metals tested outperformed Fe (Haber-Bosch catalyst).

Catalyst	T_m (K)	NH_3 Yield (%)	Energy Yield (g-NH_3/kWh)	Energy Cost (MJ/mol)	Binding Energy on Surface (in Bulk) (kJ/mol)	
					N	*H*
Ni	1728	34.1	0.41	147	-446 (-376)	-266 (-207)
Sn	505	28.8	0.35	174	-	-
Au[a]	1338	19.1	0.22	263	-168 (-42)	-193 (-100)
Ag[a]	1235	18.6	0.22	271	-155 (-130)	-197 (-153)
In[a]	430	17.7	0.22	283	-	-
Pd[a]	1828	17.6	0.21	285	-396 (-317)	-270 (-215)
Cu[a]	1358	16.7	0.20	301	-296 (-247)	-231 (-174)
Ga[a]	303	11.2	0.14	451	-410 (-389)	-172 (-139)
Fe[a]	1811	9.5	0.12	532	-705 (-213)	-323 (-82)
[a]**Metals also run in our previous work. (a) Ref 1 J. Shah, W. Wang, A. Bogaerts, Maria L. Carreon*, *ACS Appl. Energy Mater.* 2018, *1*, 4824-4839; (b) Ref 2 J. Shah, J. Harrison, Maria L. Carreon*, *Catalysts* 2018, *8*, 437.**						
Data from Haber-Bosch Process						
Fe[c,d]	1811	8-15%	500	0.5	-705 (-213)	-323 (-82)

[c]**Reference:** H.-H. Kim, Y. Teramoto, A. Ogata, H. Takagi, T. Nanba, *Plasma Chem. Plasma Process.* **2016**, *36*, 45-72. [d]To achieve such yields a minimum production capacity of 100 ton/day is required. The process occurs at high temperature(450-600°C) & High Pressure (150-350 bar). The major limitation in this process is scaling down & catalyst regeneration (Iron).

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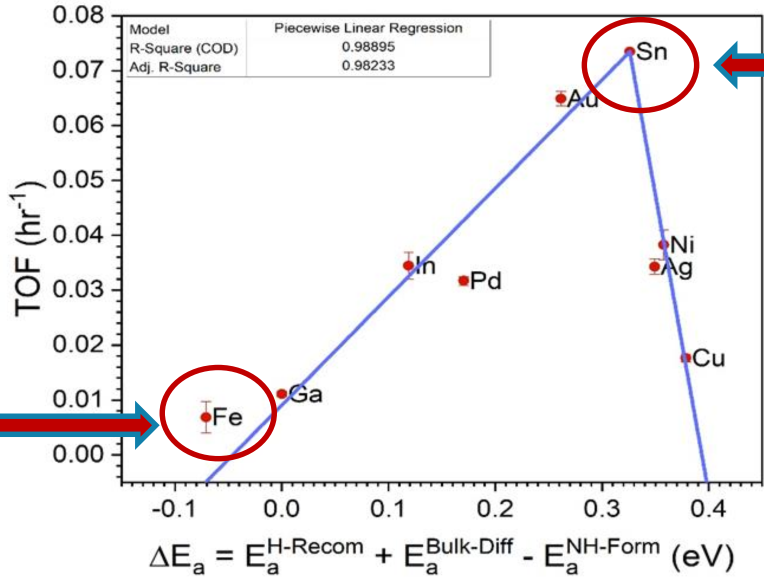
Finding new materials through DFT and experimental results

Subtracted activation energy of <u>desired reaction</u> from the total activation energy of **<u>undesired reactions</u>** (**Activation energy of H_2 recombination** + **Activation energy of Bulk diffusion**) – **Activation energy of N-H formation**.



New material

Old material

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Vacuum discharges simultaneously **competing parallel reactions:**

N-H formation via E-R, **H_2 formation via E-R** and **H-bulk diffusion**.

*Shah Javishk, Gorky, Psarras Peter, Seong Bomsaerah, Gomez-Gualdron Diego, **<u>Carreon Maria L.*</u>** Ammonia yield enhancement by hydrogen sink effect during plasma catalysis. ChemCatChem, **2020**, 12 (4), 1200-1211.*

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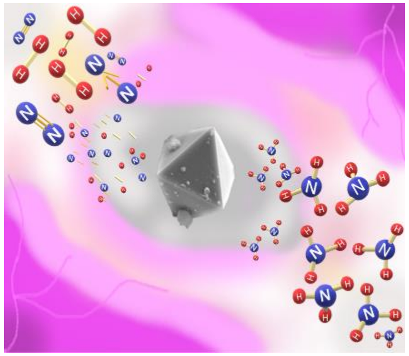
Ammonia Sorption Capacity of MOFs in plasma



- Ni-MOF-74 displayed a decrease in ammonia yield as a function of time.
- Behavior explained by the high ammonia sorption capacity over Ni based MOFs.
- In our study, as the reaction proceeded, the ammonia molecules start to fill the MOF pores reducing the ammonia detection in the exhaust gases.
- The total ammonia loading was found to be 3.14 mmol/g-MOF.
- Microporous molecular sieve crystals composed of inorganic (SAPO-34), hybrid (ZIF-8, and ZIF-67), and organic (CC3) walls with uniform crystallographic limiting pore apertures (3.4-3.8 Å range).
- ZIF-8 and ZIF-67 displayed the best catalytic performance. The dipole-dipole interactions between the polar ammonia molecule and the polar walls of ZIF-8 and ZIF-67 led to relatively low ammonia uptakes and storage capacity, and to the high observed ammonia synthesis rates.

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Shah, Javishk, Wu, Ting, Lucero, Jolie, Carreon, Moises A., ***Carreon, Maria L.*,*** *Nonthermal Plasma Synthesis of Ammonia over Ni-MOF-74, ACS Sustainable Chemistry & Engineering, 7(1),* ***2018,*** *377-383.*

Gorky, Fnu, Lucero, Jolie, Crawford, James, Carreon, Moises A., and ***Carreon, Maria L.**** Plasma Assisted Ammonia Synthesis over Microporous Crystalline Molecular Sieves, ACS Catalysis, *Under review*.

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Plasma catalysis and other environmental reactions

- The main appeal of plasma-assisted catalysis is the alternative way to activate the "source gas" by collision with electrons. This can be exploited to help activate strong bonds(e.g. C-H bond in CH_4 and N≡N bond in N_2).

- Abatement of volatile organic compounds (VOCs) emitted from various industries by decomposing VOCs into harmless substances such as CO_2 and H_2O has been performed when employing NTP.

- NTP VOCs decomposition benefits: (1) energy efficiency higher than that of thermal oxidation. (2) operates at atmospheric pressure and room temperature. (3) can be easily integrated with various packing materials. (4) It can be quickly switched on/off.

- **This can serve as a motivation to explore other catalytic systems such as methane into CO_2!**

Khan, Faisal I., and Aloke Kr Ghoshal. "Removal of volatile organic compounds from polluted air." Journal of loss prevention in the process industries 13, no. 6 (2000): 527-545; C. Dai, Y. Zhou, H. Peng, S. Huang, P. Qin, J. Zhang, Y. Yang, L. Luo, X. Zhang, Current progress in remediation of chlorinated volatile organic compounds: A review, J. Ind. Eng. Chem. 62 (2018) 106–119.

Atmospheric restauration: methane removal

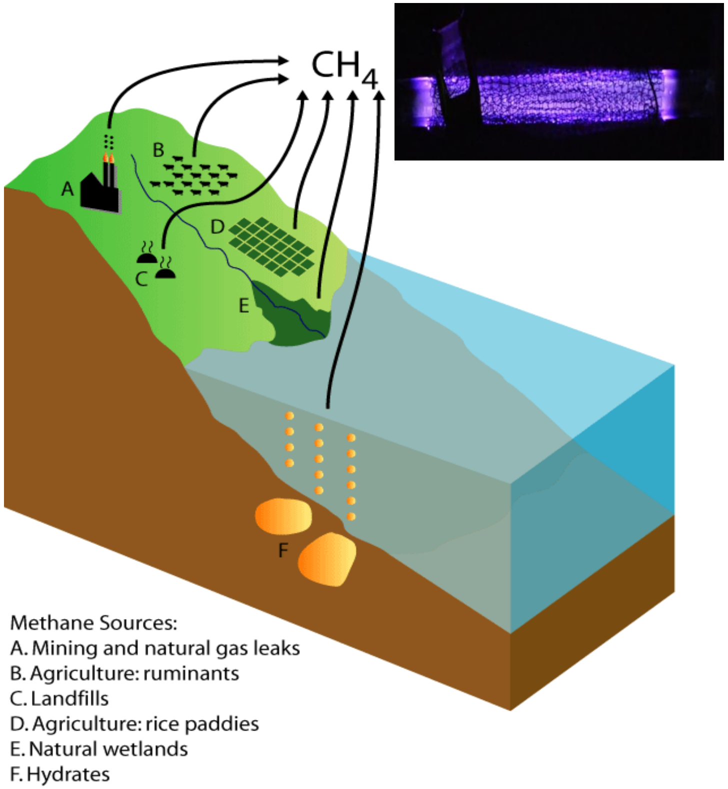
- CH_4 is the most dominant anthropogenic greenhouse gas (after CO_2).
- Methane react with nitrogen oxides leading to tropospheric ozone pollution.
- Methane is 84 times more potent than CO_2 over the first 20 years after release and ~28 times more potent after a century.
- Methane concentrations could be restored to preindustrial levels by removing ~3.2 of the 5.3 Gt of CH_4 currently in the atmosphere.
- Rather than capturing and storing the methane, the CH_4 could be oxidized to CO_2, a thermodynamically favorable reaction:

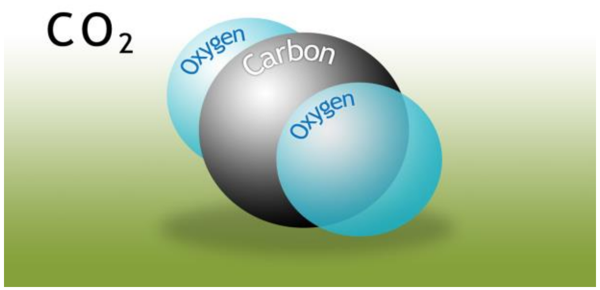
$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O;\ \Delta H_r = -803\ kJ\ mol^{-1}.$$

- The large activation barrier associated with splitting methane's C–H bond (435 kJ mol^{-1}/4.5 eV) could in principle be overcome by the right selection of NTP with a proper catalyst for such environment.
- Only plasma allows to overcome the activation barrier associated with the N-N bond (941. 69 kJ/mol-1/9.75 eV).

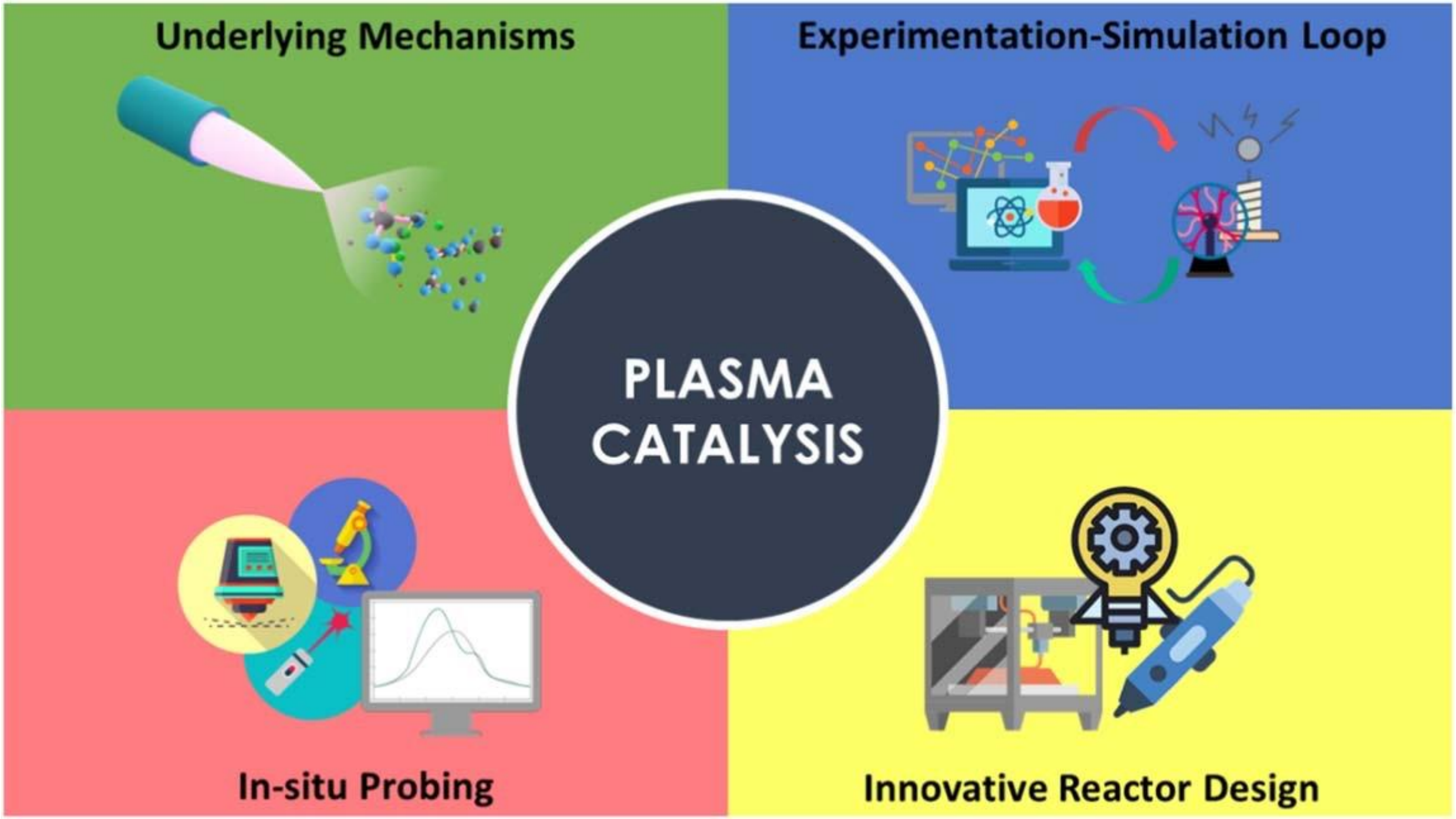
Jackson, R. B., E. I. Solomon, J. G. Canadell, M. Cargnello, and C. B. Field. "Methane removal and atmospheric restoration." Nature Sustainability 2, no. 6 (2019): 436-438; https://nvlpubs.nist.gov/nistpubs/Legacy/NSRDS/nbsnsrds31.pdf

"The synergistic effect of the right plasma-catalyst pair has been demonstrated for the synthesis of ammonia. In principle, this remarkable synergy can be exploited for other societal relevant reactions, including the oxidation of methane to carbon dioxide."





The challenges to pave the plasma catalysis future



***Carreon, Maria L**. "Plasma catalysis: a brief tutorial." Plasma Research Express 1, no. 4 (2019): 043001.*

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Questions?

"Plasma processing is born out of the need to access a parameter space in materials processing unattainable by strictly chemical methods"

Lieberman and Lichtenberg