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

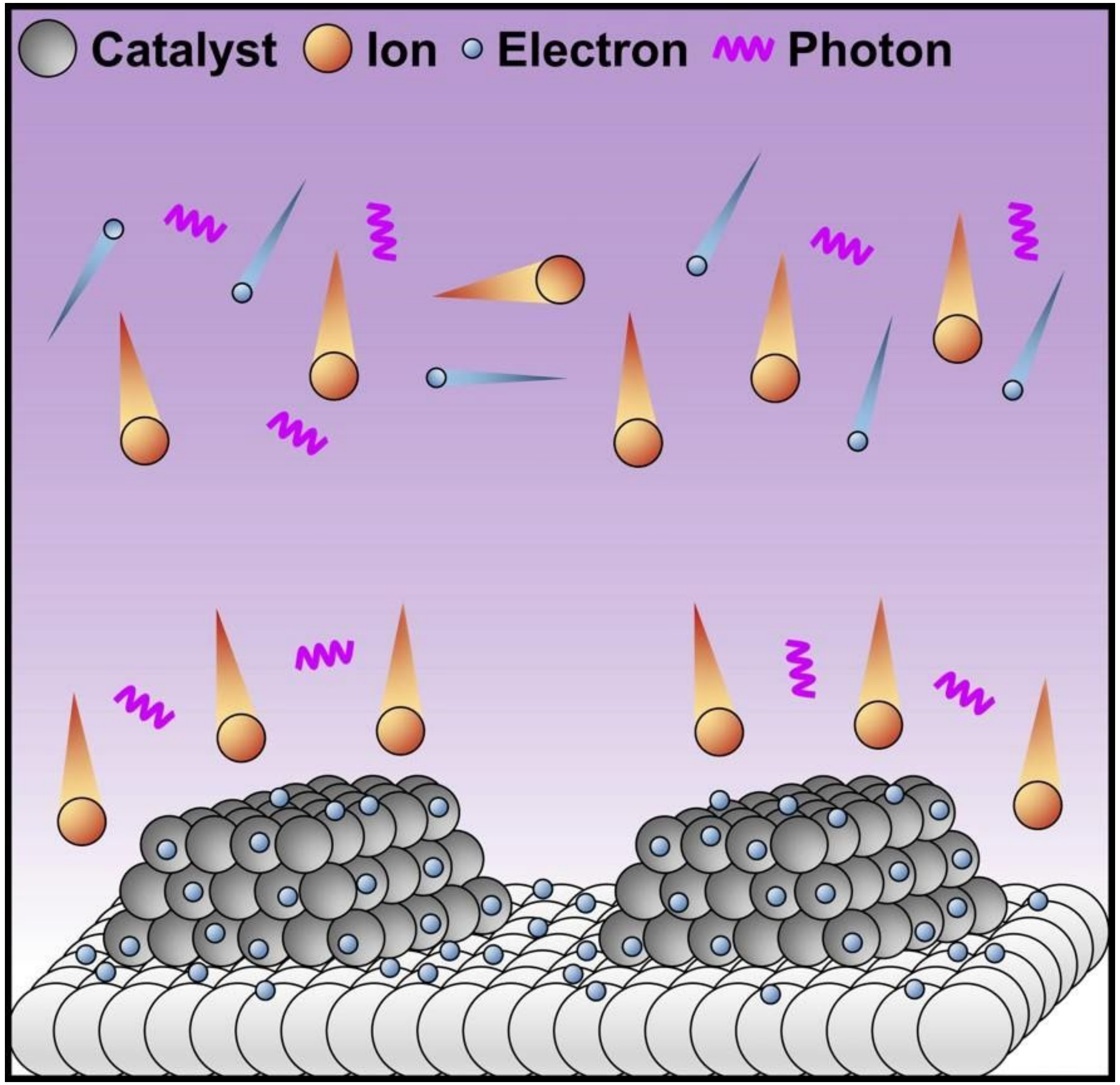
Minseok Kim

MANGOLINI GROUP

DEPARTMENT OF MECHANICAL ENGINEERING, UNIVERSITY OF CALIFORNIA, RIVERSIDE

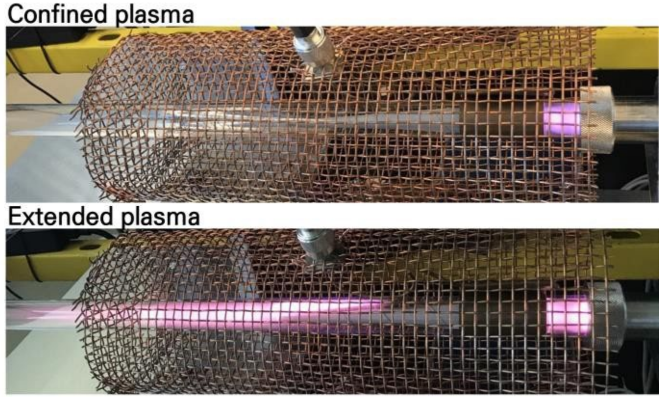
04. 24. 2024

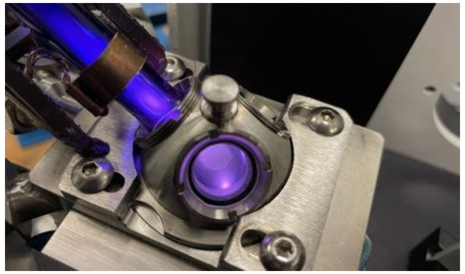
1-1. Plasma catalysis for gas conversion



Experiments with Plasmas

Gas conversion and plasma characterizations

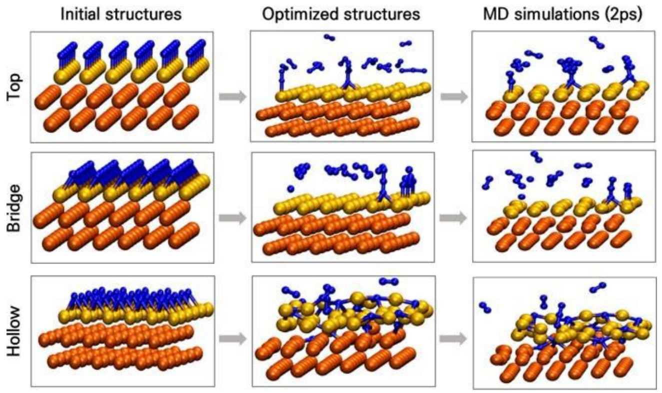


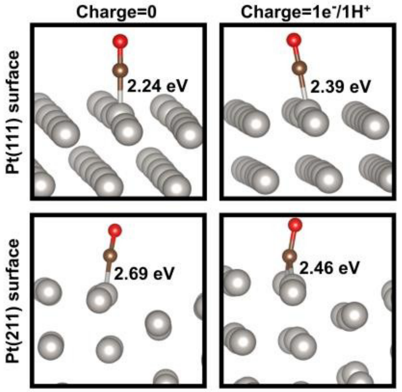


Actual power measurements
Si-based detector for light intensity
Capacitive prove for plasma density

Quantum Calculations

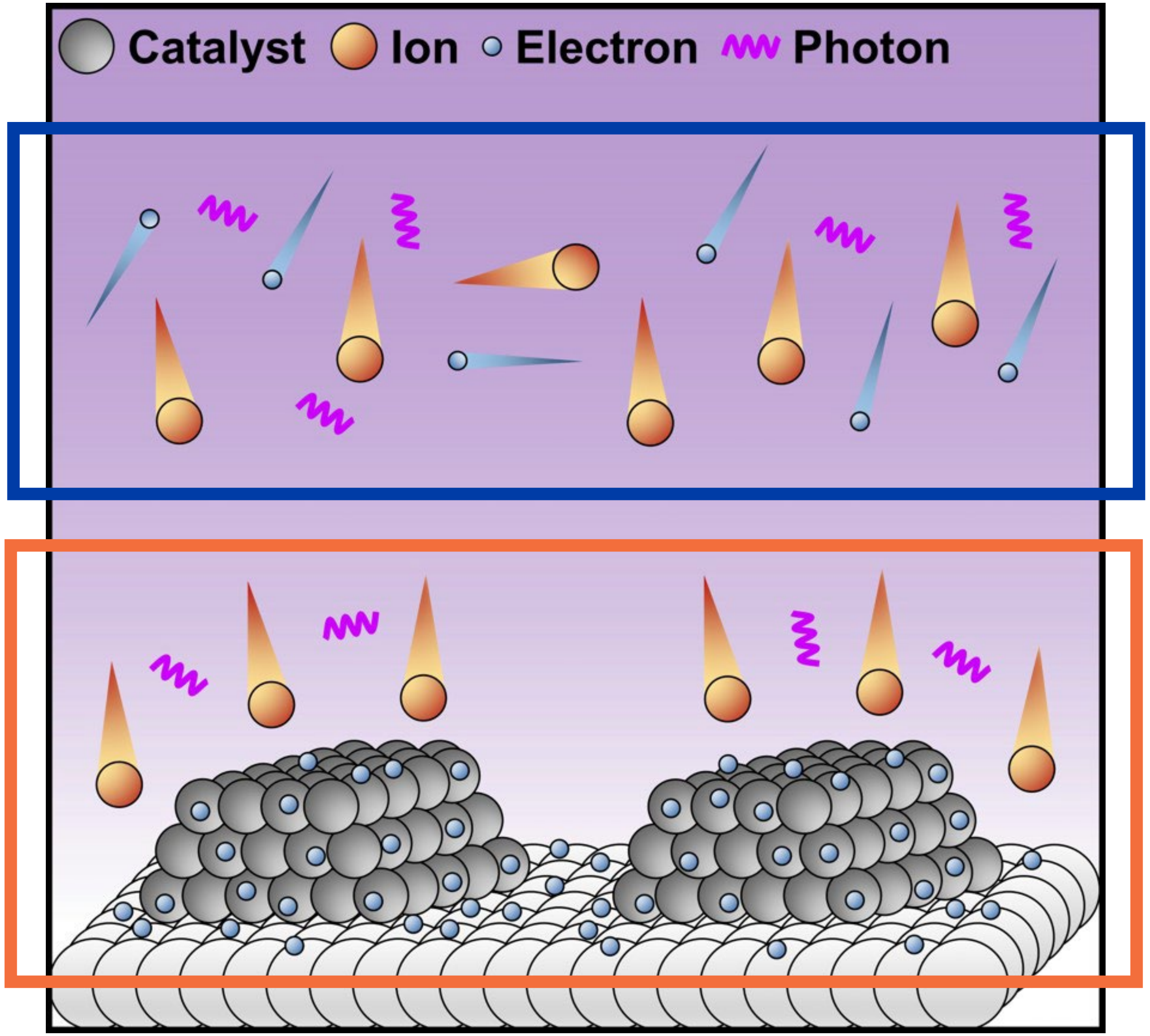
Density Functional Theory (DFT) calculations





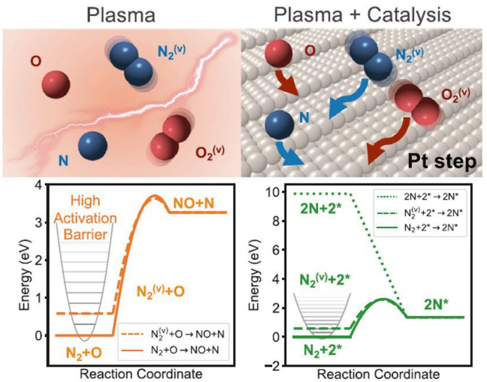
1. Ma, H. *et al.* *Nat. Commun.* **13**, 402 (2022).
2. Kim, D. Y. *et al.* *J. Am. Chem. Soc.* **144**, 14140–14149 (2022).
3. Gunasooriya, G. T. K. K. *et al.* *ACS Catal.* **7**, 1966–1970 (2017).
4. Berrospe-Rodriguez, C. *et al.* *Phys. Rev. Appl.* **15**, 024018 (2021).

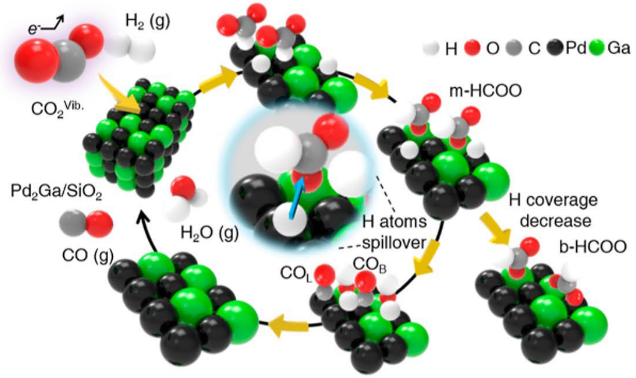
1-2. Plasma-surface interaction



Pathway 1 in the BULK PLASMA

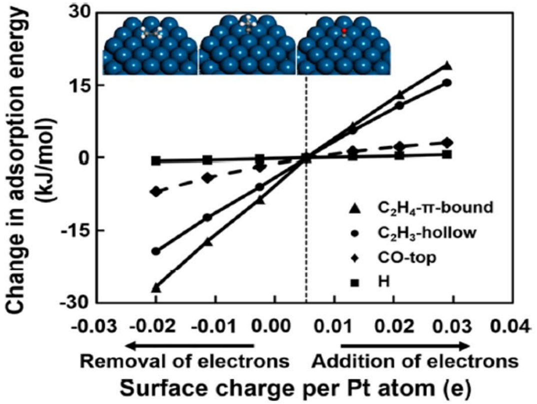
Vibrational excitation of molecules (e.g., N_2 and CO_2)[1,2]

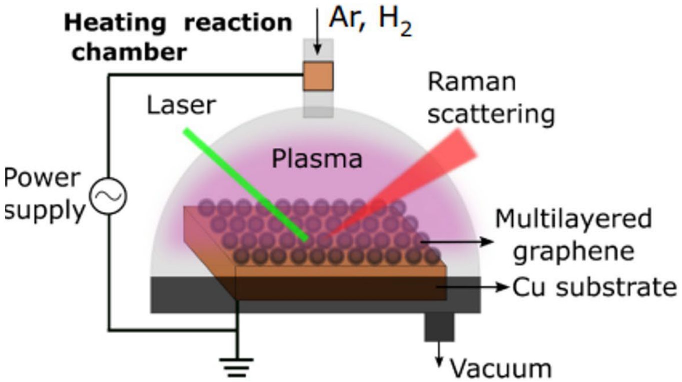




Pathway 2 on the SURFACE OF CATALYST

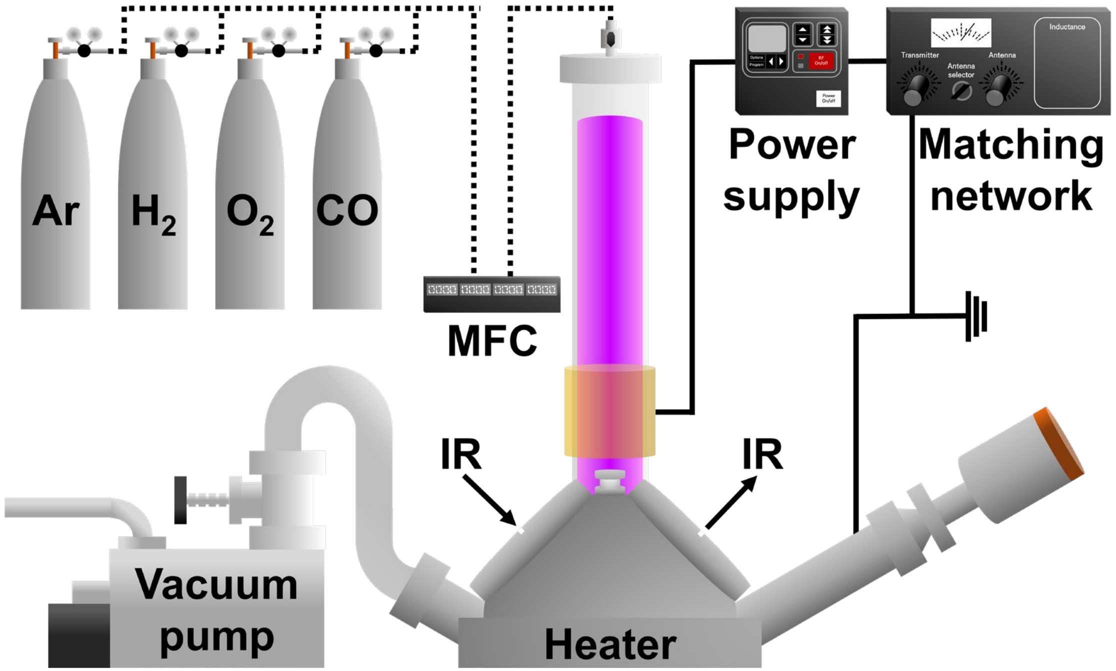
Activation at the plasma catalyst interface[3,4]





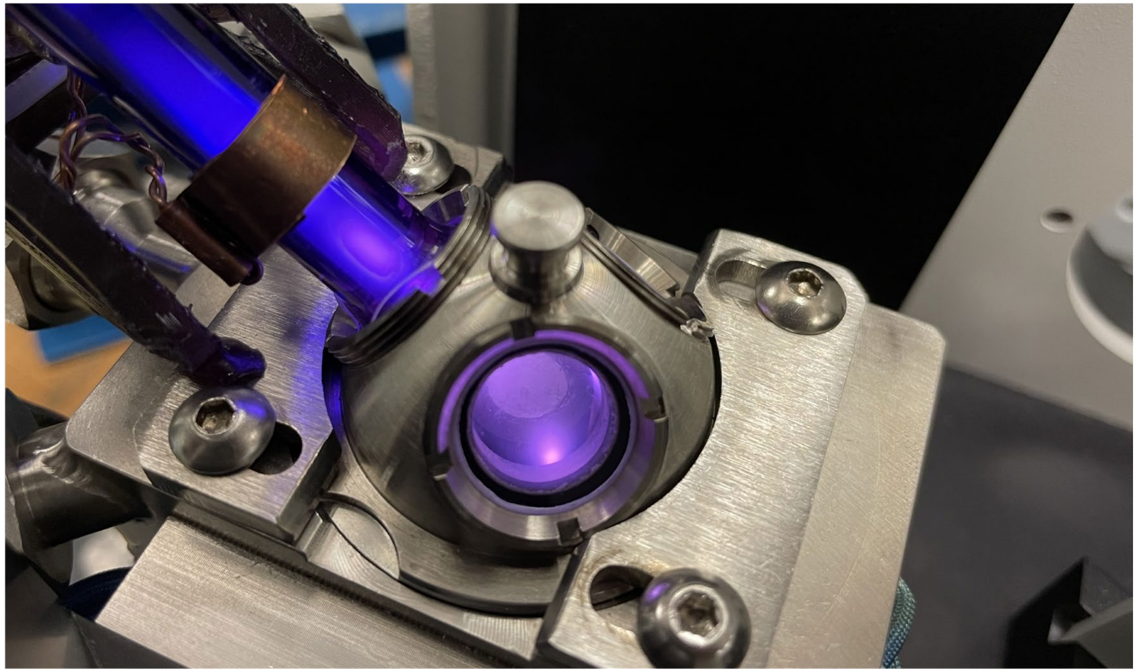
2-1. *in situ* Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS)

2-1-1. Temperature Programmed Desorption (TPD)



Experimental conditions	
Flow rate of Ar [sccm]	20
Pressure [torr]	3.7
Ramp rate [10 K/min]	10
RF input power [W]	7, 15, 30, and 45

Argon plasma while operating

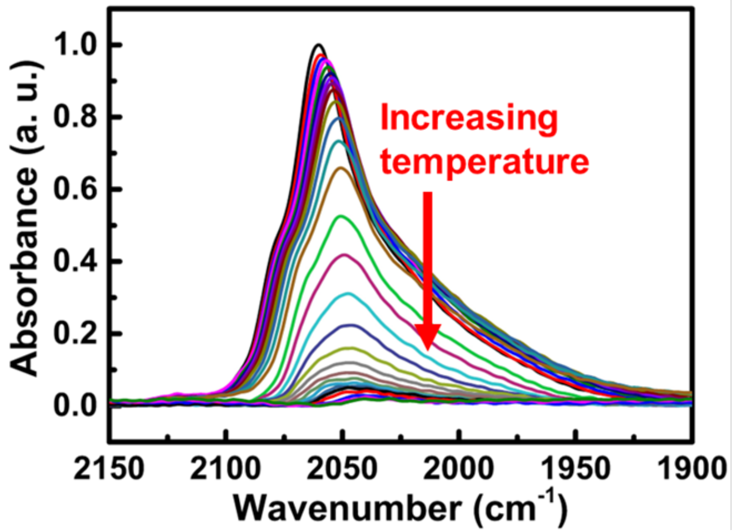


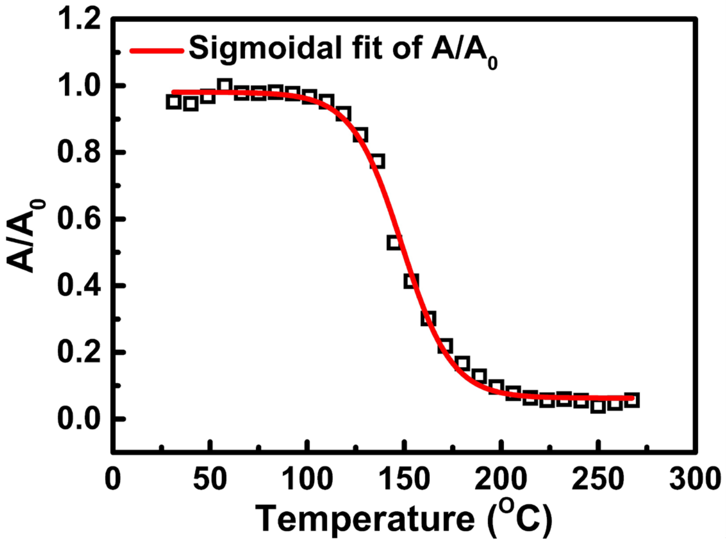
Catalysts: 1% Pt/Alumina

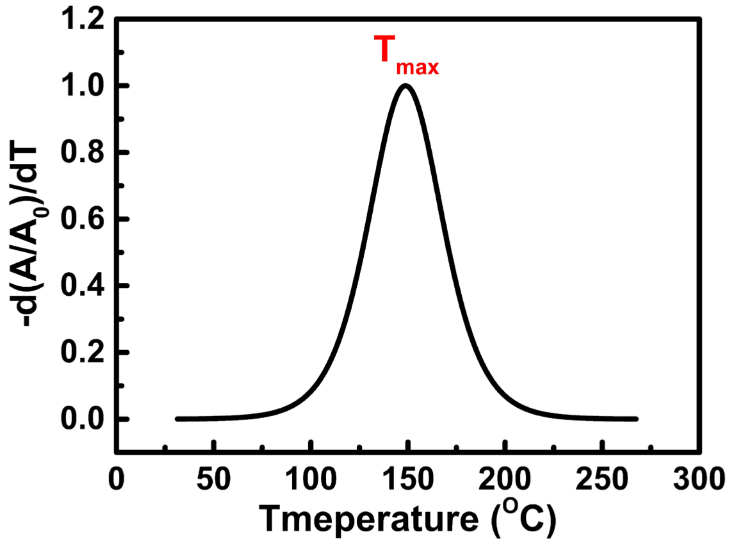
[1]Redhead, P. A. Vacuum 12, 203–211 (1962).

2-1. *in situ* Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS)

2-1-2. Redhead analysis through TPD[1]







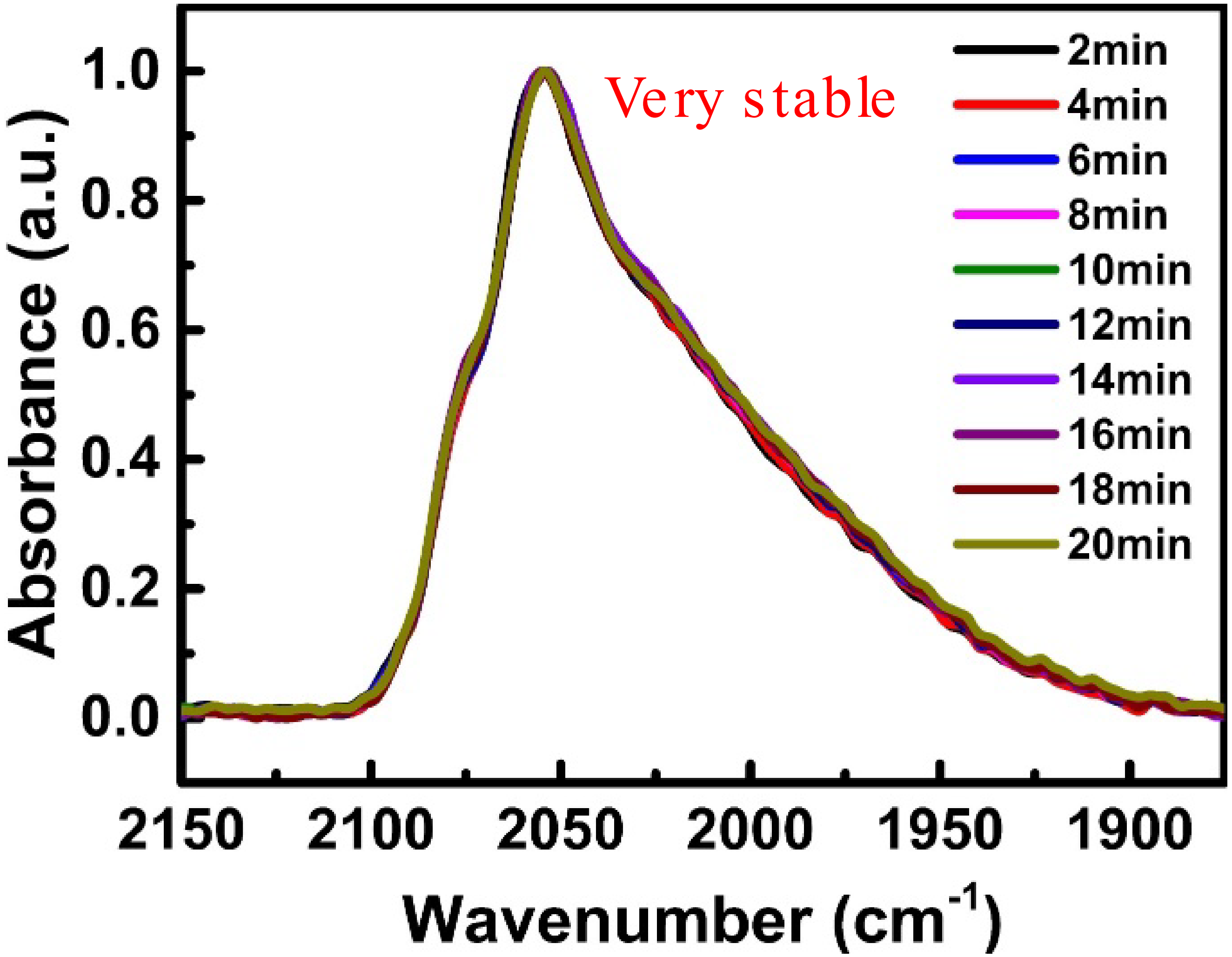
$$Binding\ energy = RT_{max}\left[\ln\left(\frac{\upsilon T_{max}}{\beta}\right) - 3.46\right]$$

$R = gas\ constant\ (= 8.3145\ J/mol \cdot K)$

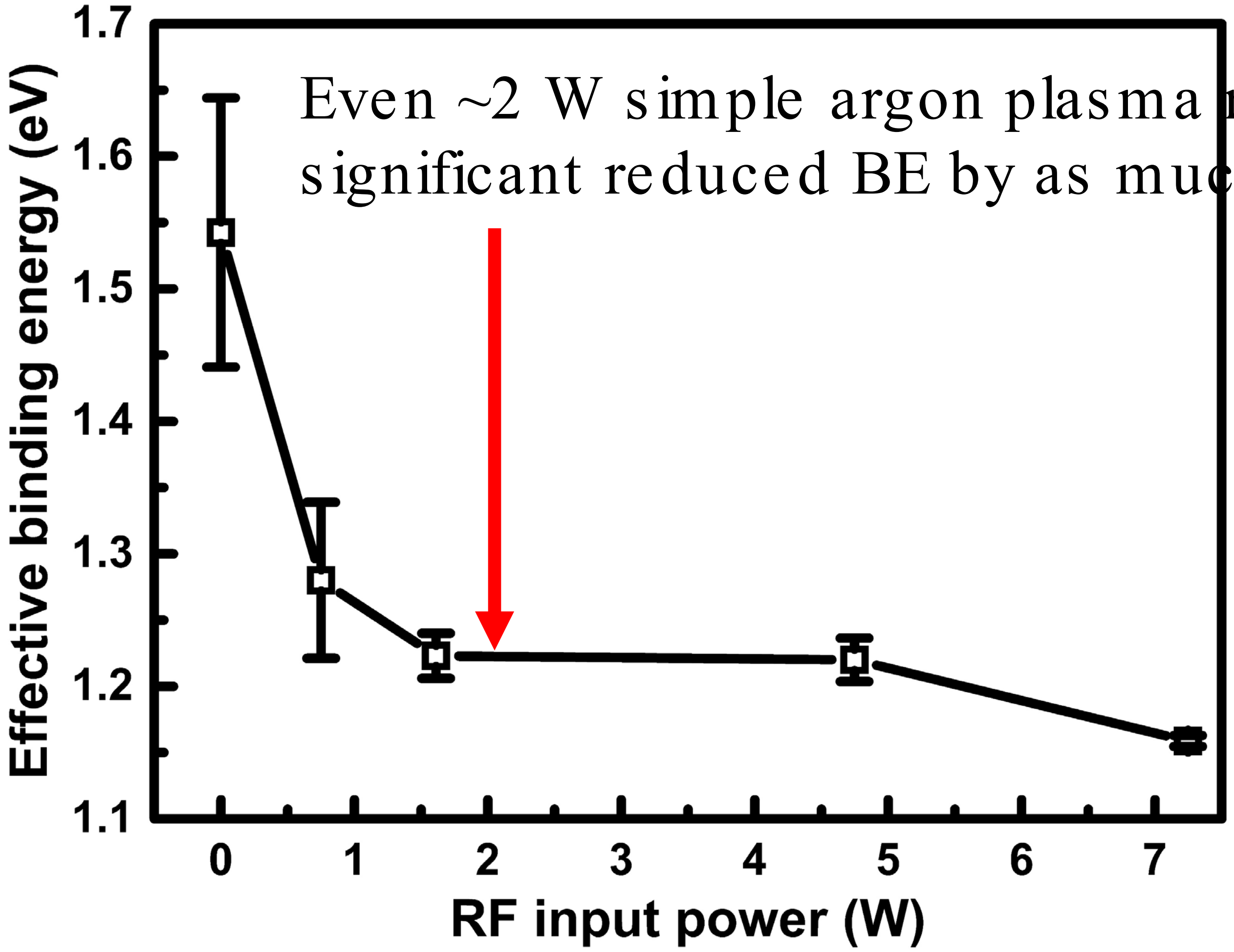
$\upsilon = Pre - exponential\ factor\ (= 10^{13}\ s^{-1})$

$\beta = ramp\ rate\ (= 10\ K/min)$

3-1. Stable chemisorption of CO on Pt



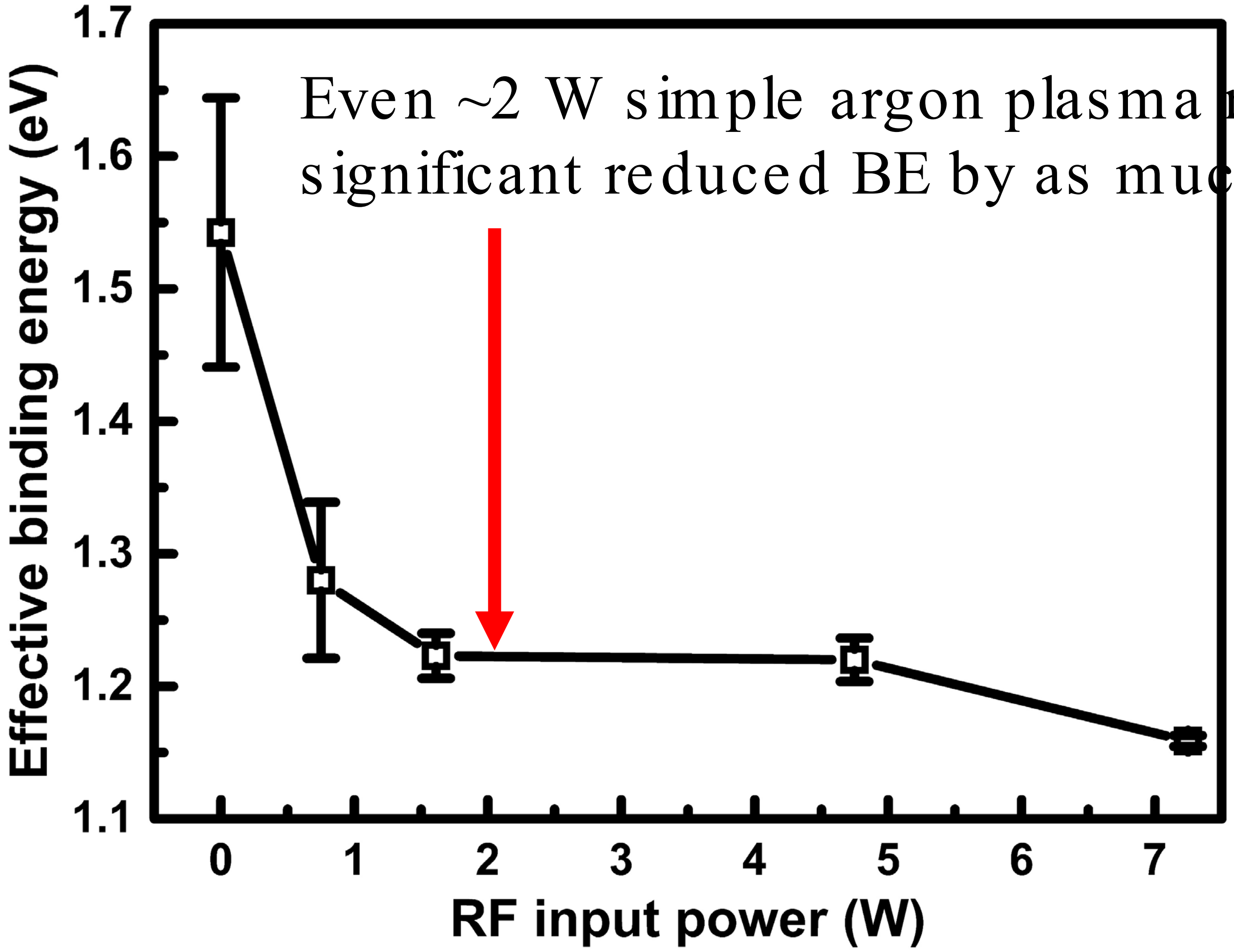
3-2. Reduced binding energy (BE) with argon plasma exposure

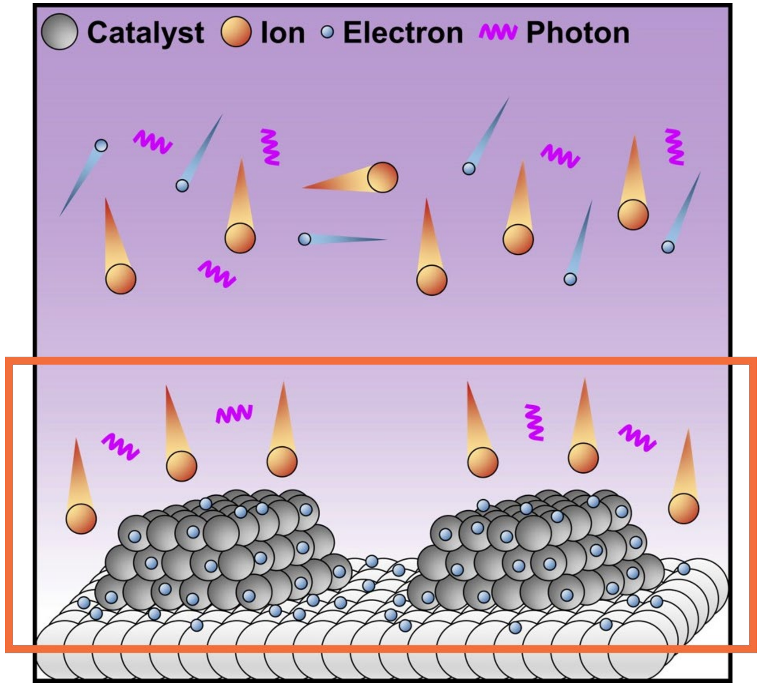


Even ~2 W simple argon plasma results in significant reduced BE by as much as ~0.3 eV.

3-2. Reduced binding energy (BE) with argon plasma exposure

Even ~2 W simple argon plasma results in significant reduced BE by as much as ~0.3 eV.

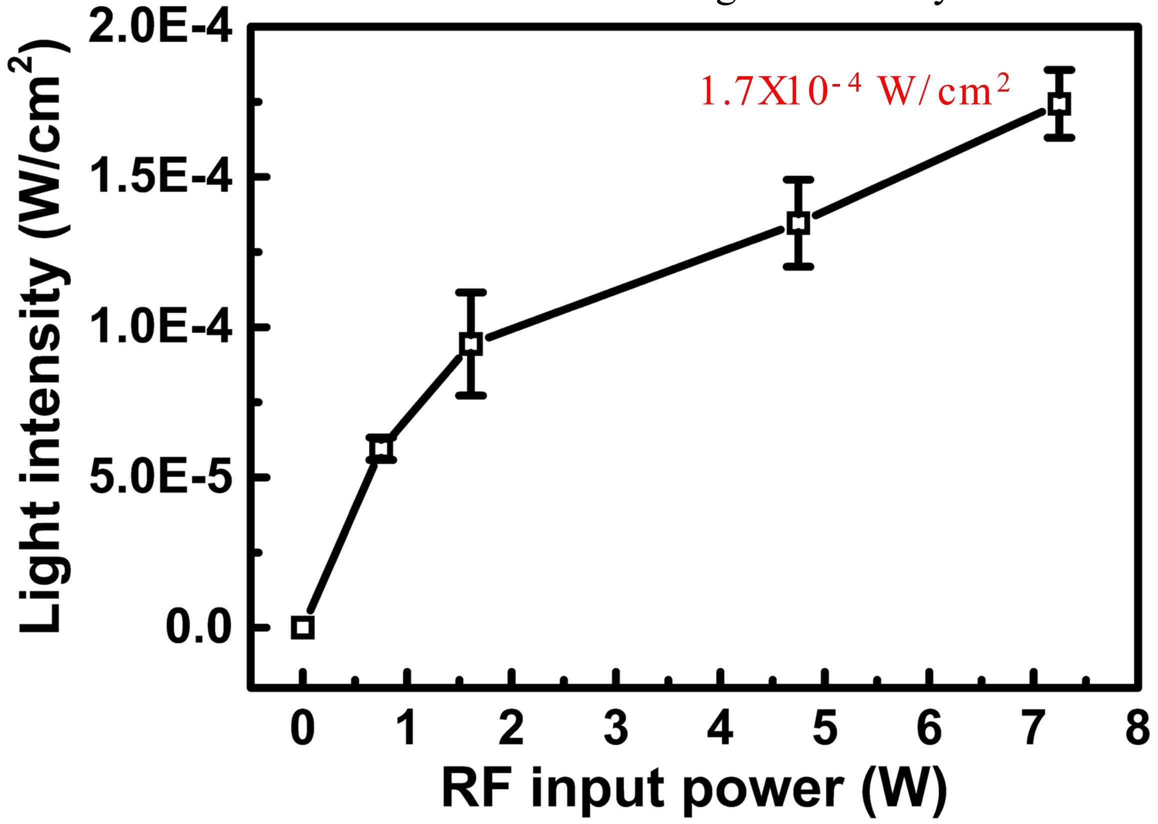


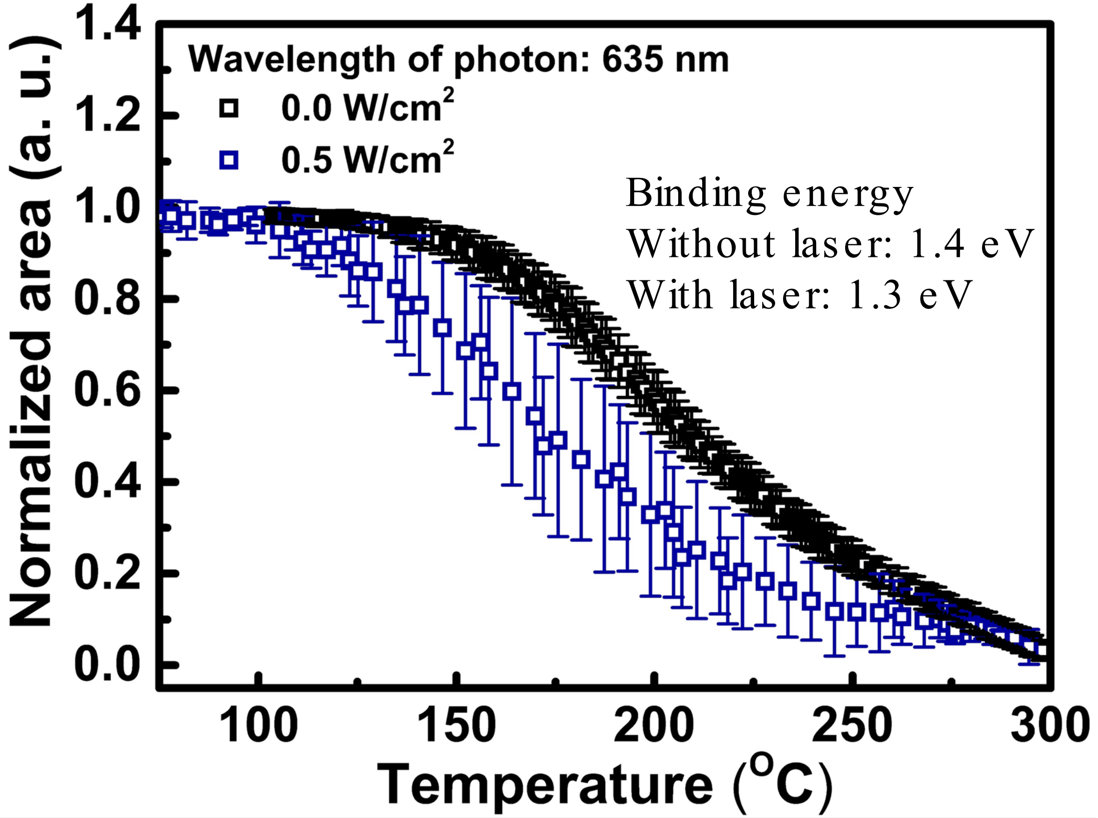


Photons? Ions?
Surface charging?

3-3. Light intensity measurements

*Si-based detector for light intensity measurements

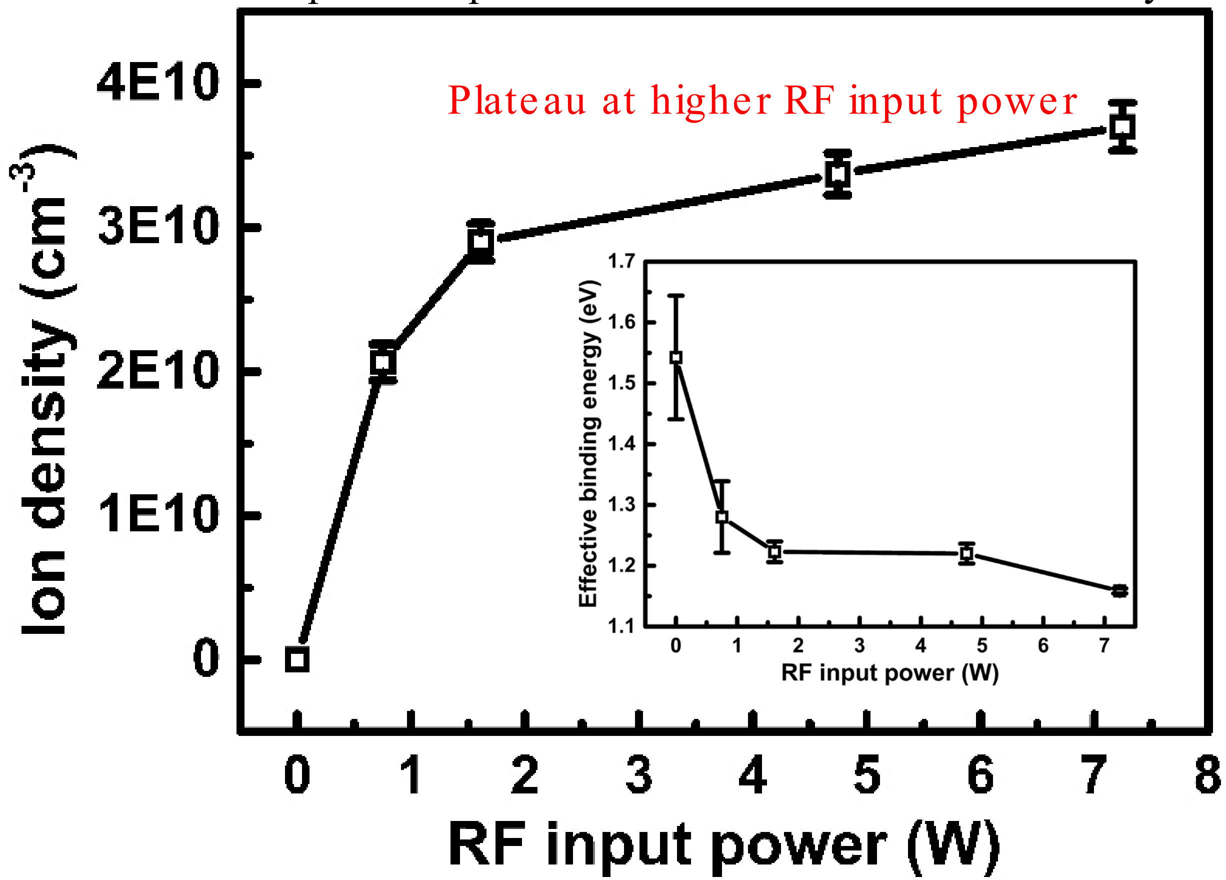


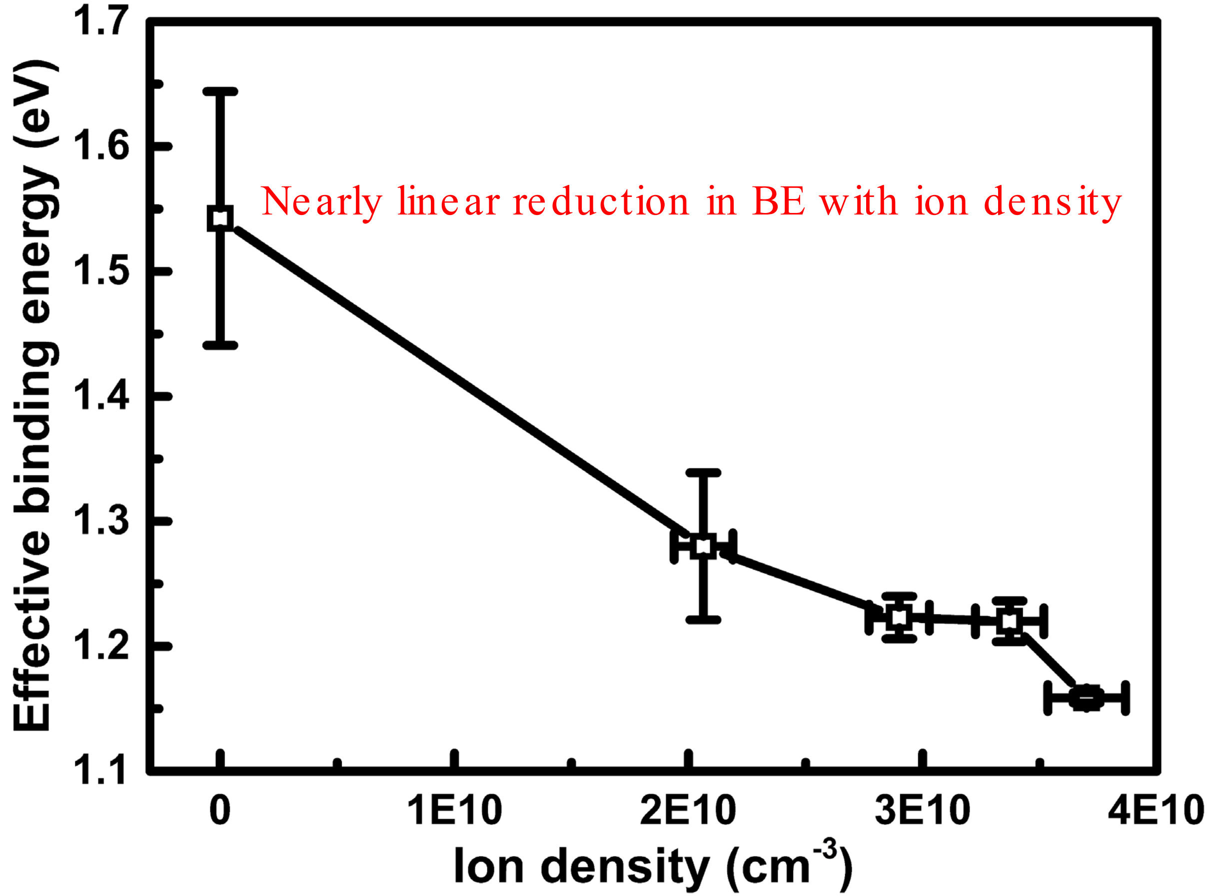


$0.5\ W/cm^2$ required
to reduce ~0.1 eV of BE

3-3. Ion density (plasma density) measurements

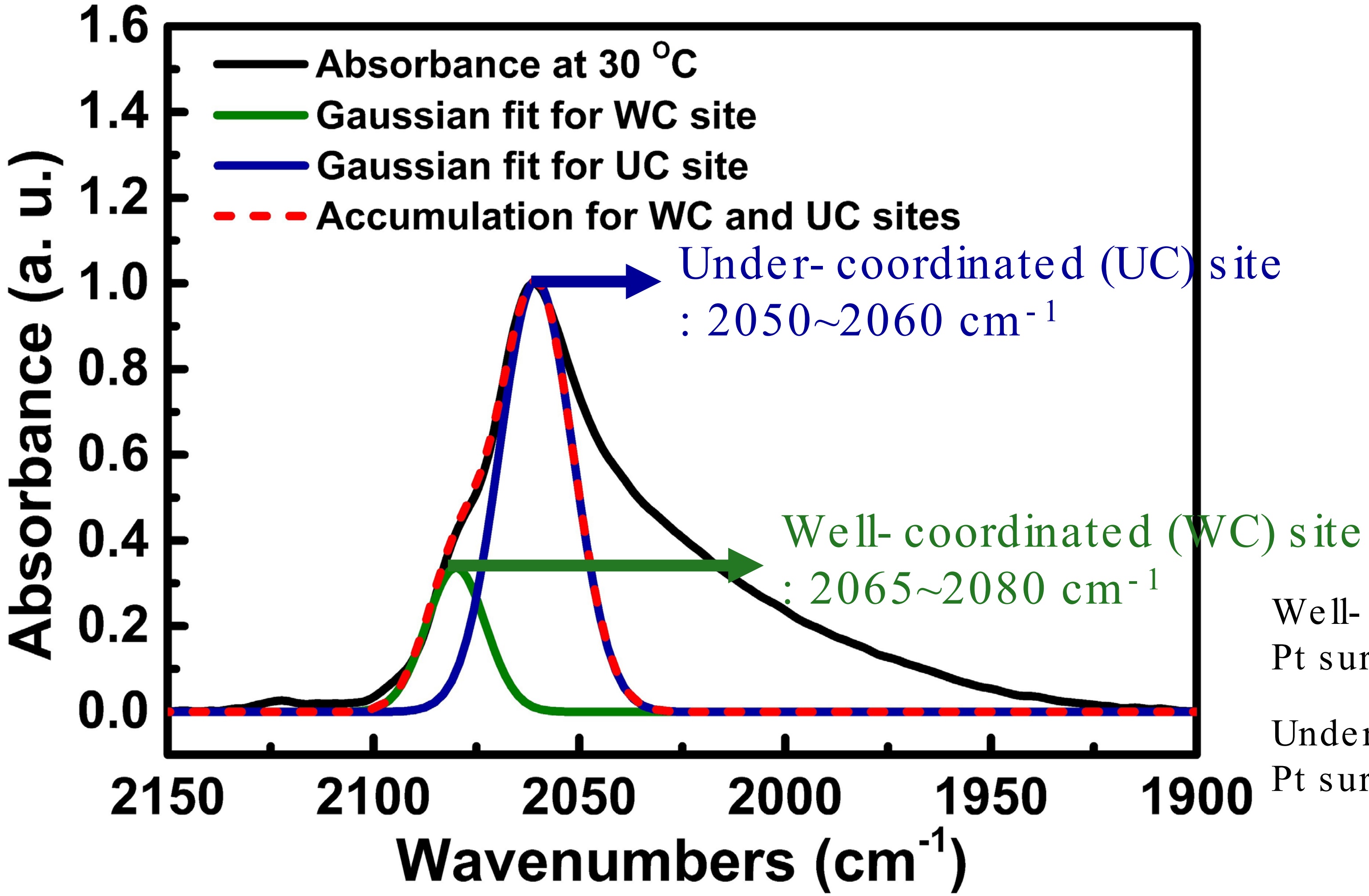
*Capacitive prove measurements for ion density

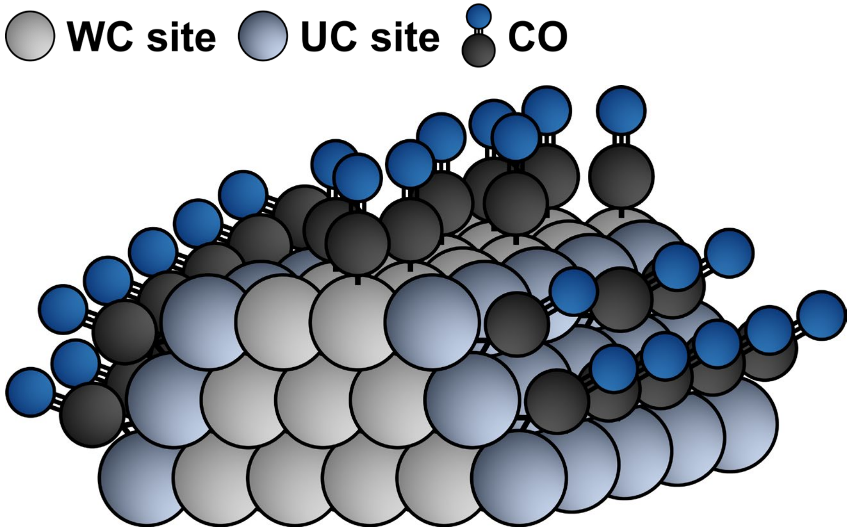




Ion bombardment induce surface heating

3-4. Deconvolution of spectrum



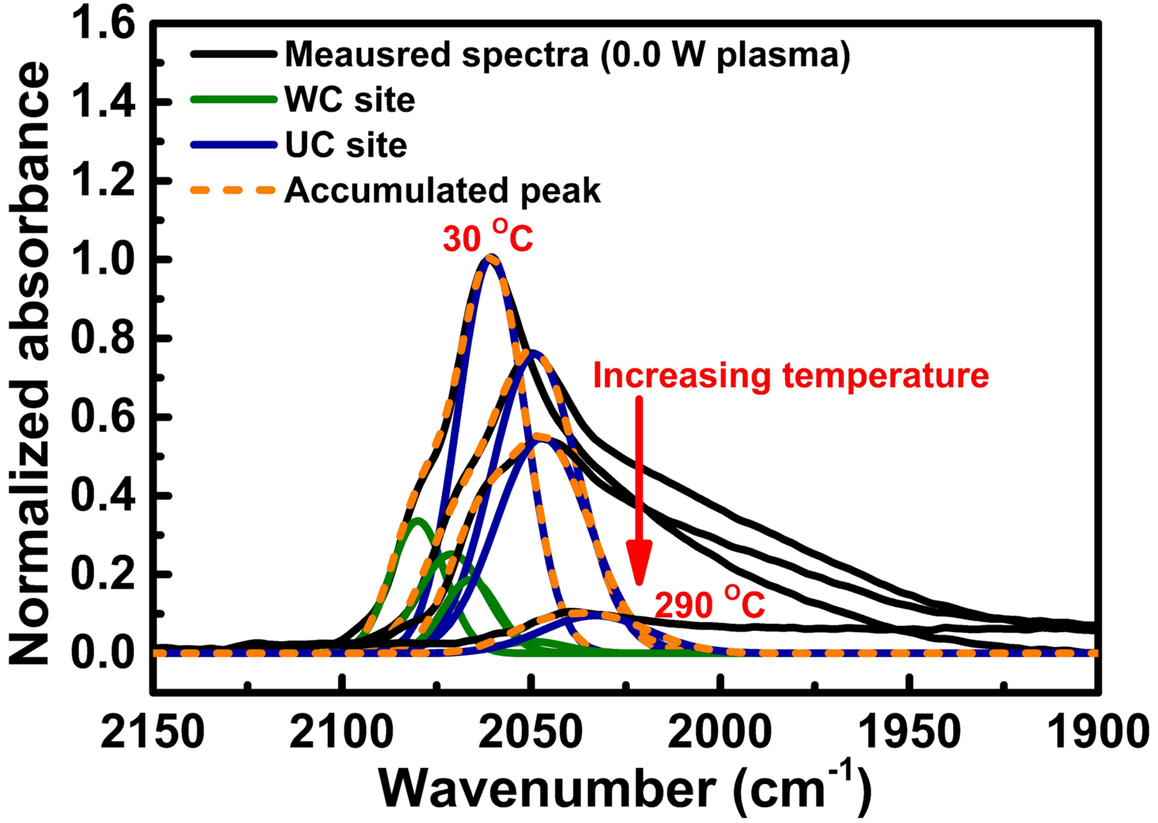


Well-coordinated (WC) site:
Pt surface sites with coordination numbers of 8 or 9

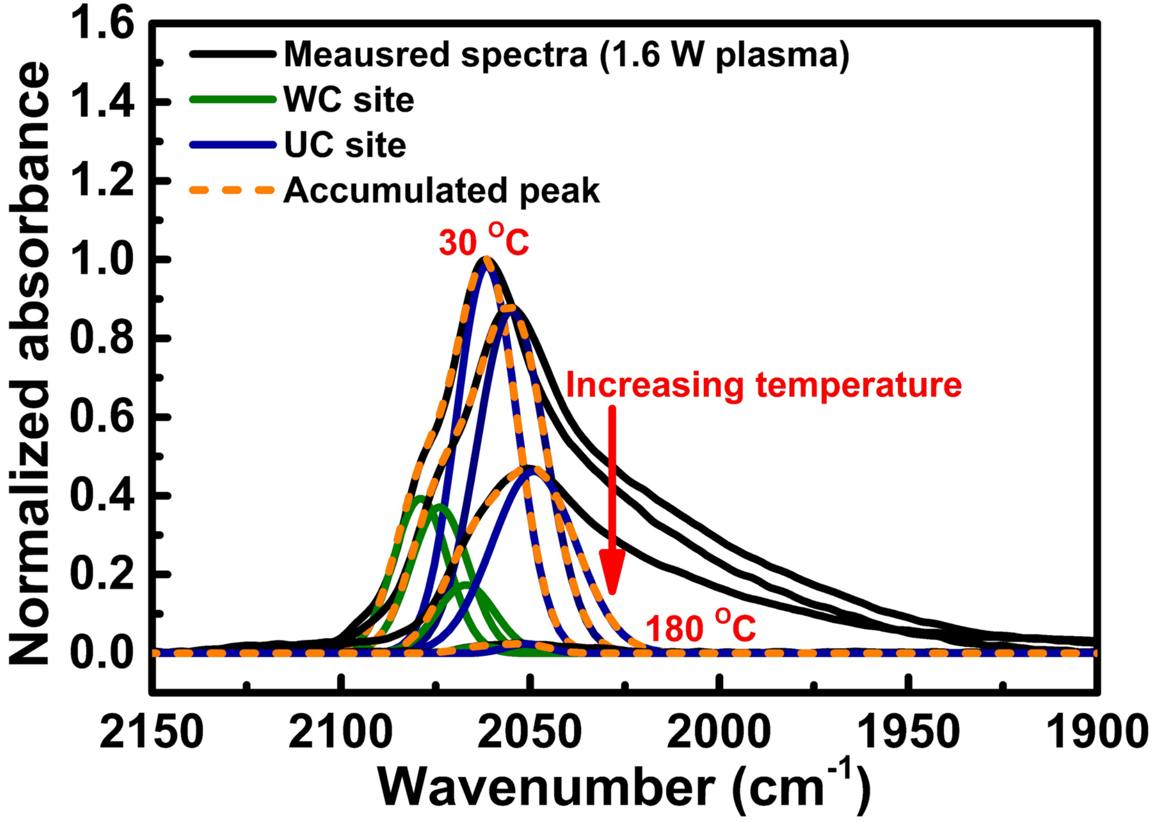
Under-coordinated (UC) site:
Pt surface sites with coordination numbers <8

3-5. Reduction in BE of WC and UC site

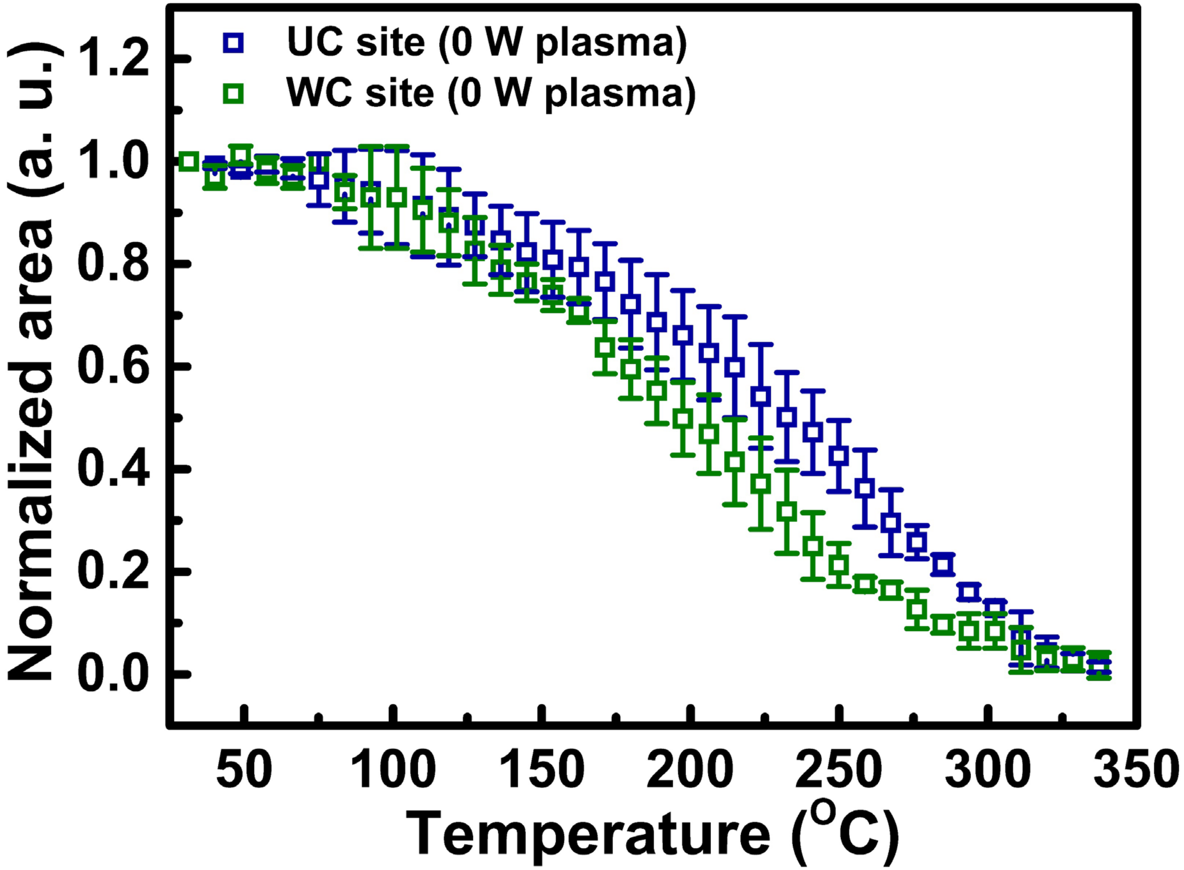
Without plasma



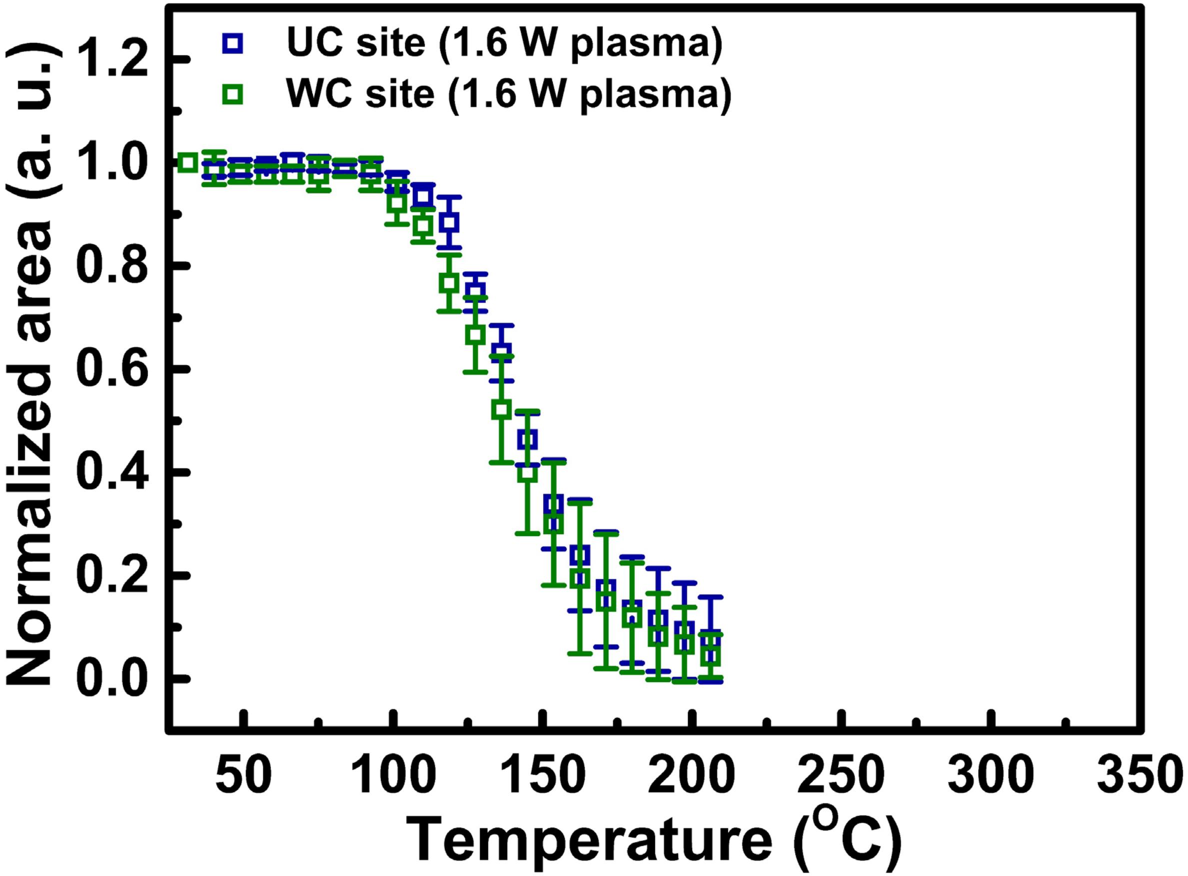
With plasma



3-5. Reduction in BE of WC and UC site



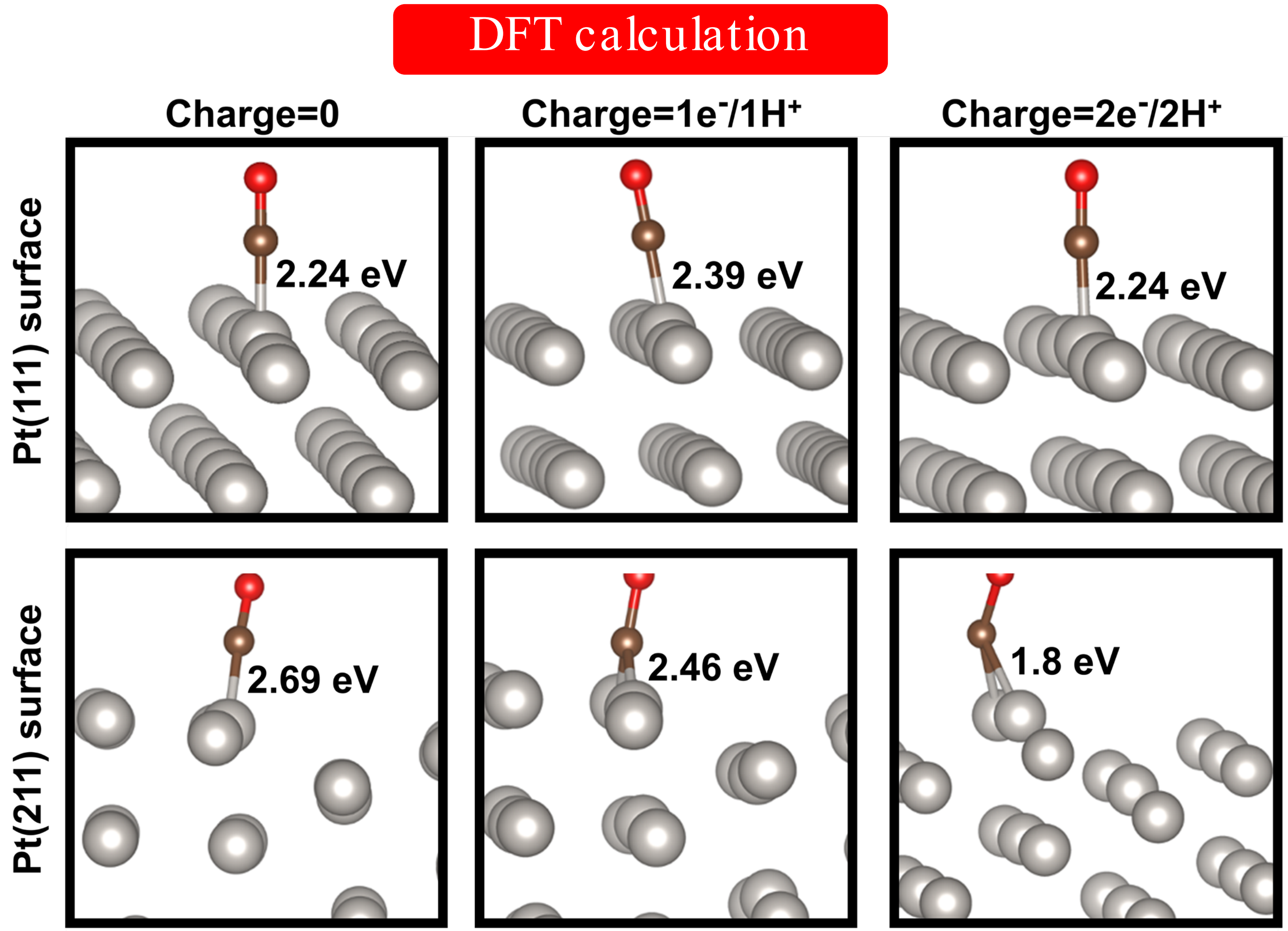
UC: 1.55 ± 0.08 eV/molecule
WC: 1.38 ± 0.05 eV/molecule

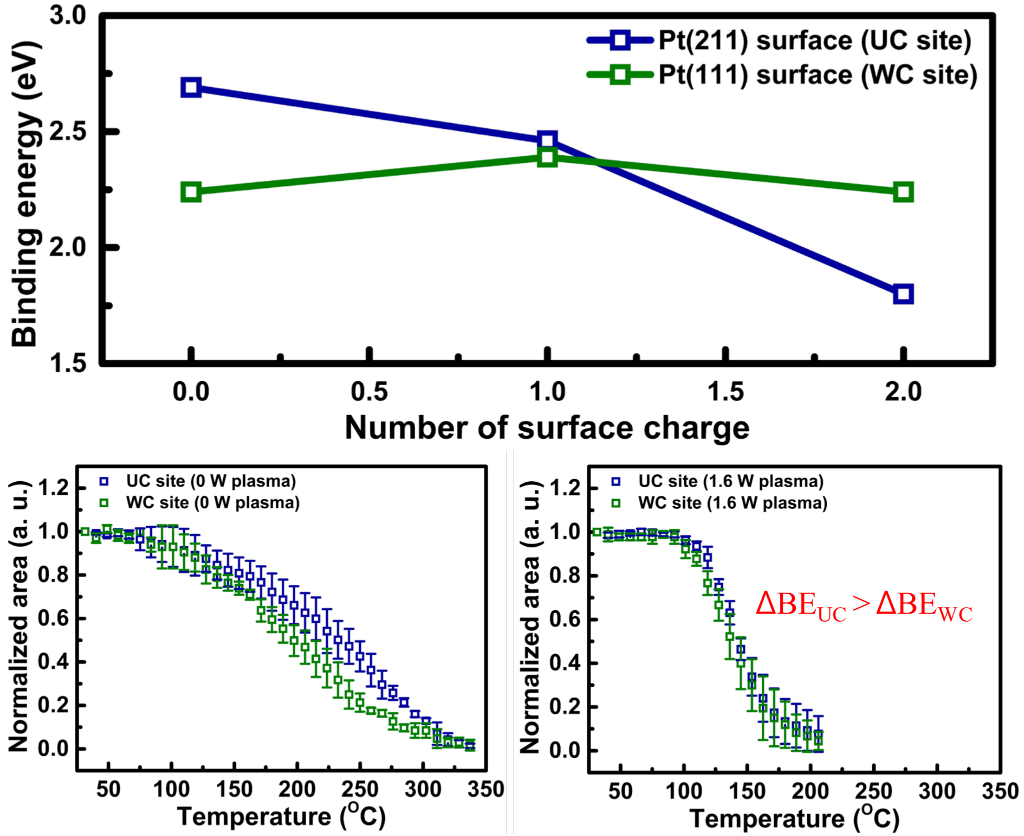


UC: 1.21 ± 0.01 eV/molecule
WC: 1.21 ± 0.01 eV/molecule

$\Delta BE_{UC} > \Delta BE_{WC}$

3-6. Effect of surface charges

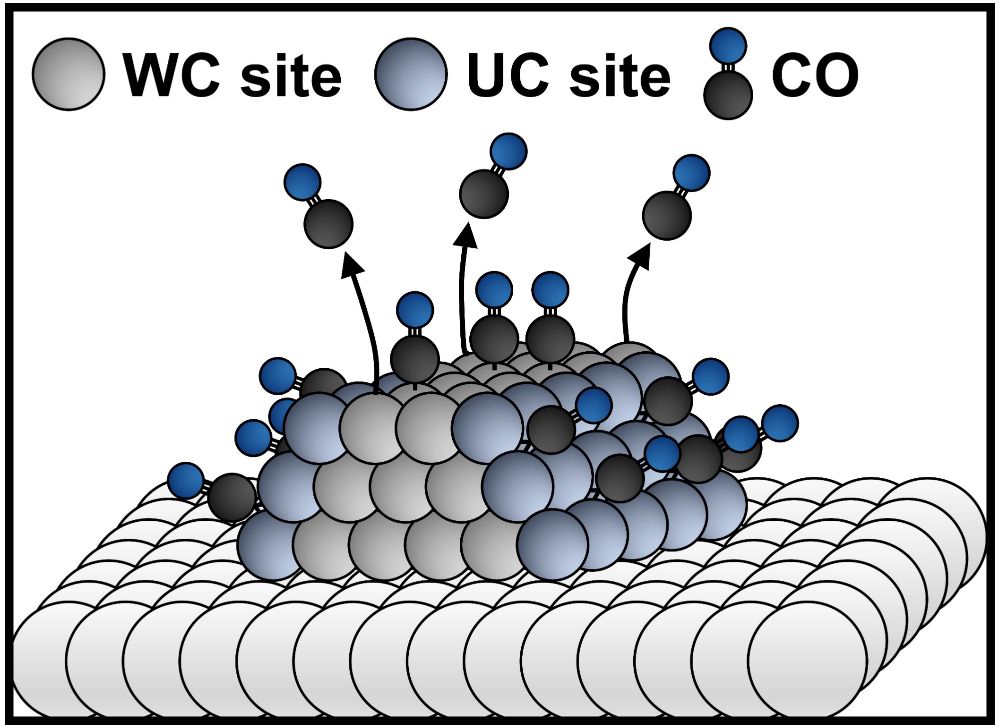




Selective desorption of CO on UC sites by surface charges

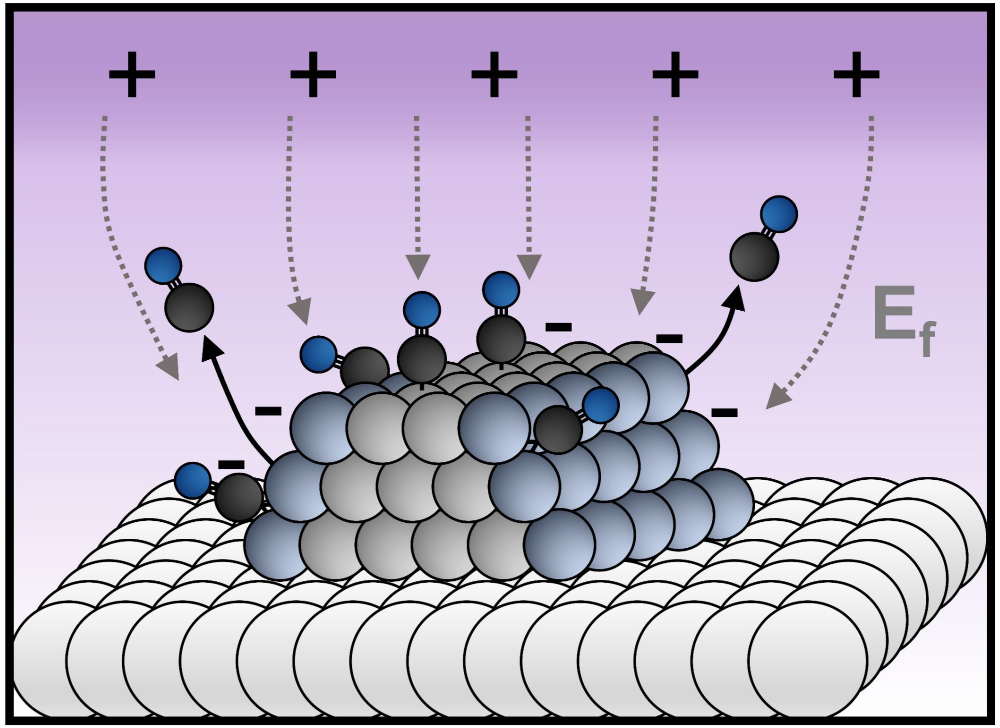
3-7. Overall insight on plasma-induced desorption of CO on Pt

Without plasma



Higher binding energy for UC site than WC site
(Without plasma exposure)

With plasma

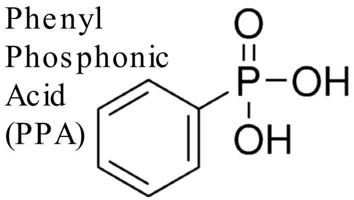


Almost same binding energy for both sites
(With argon plasma exposure)

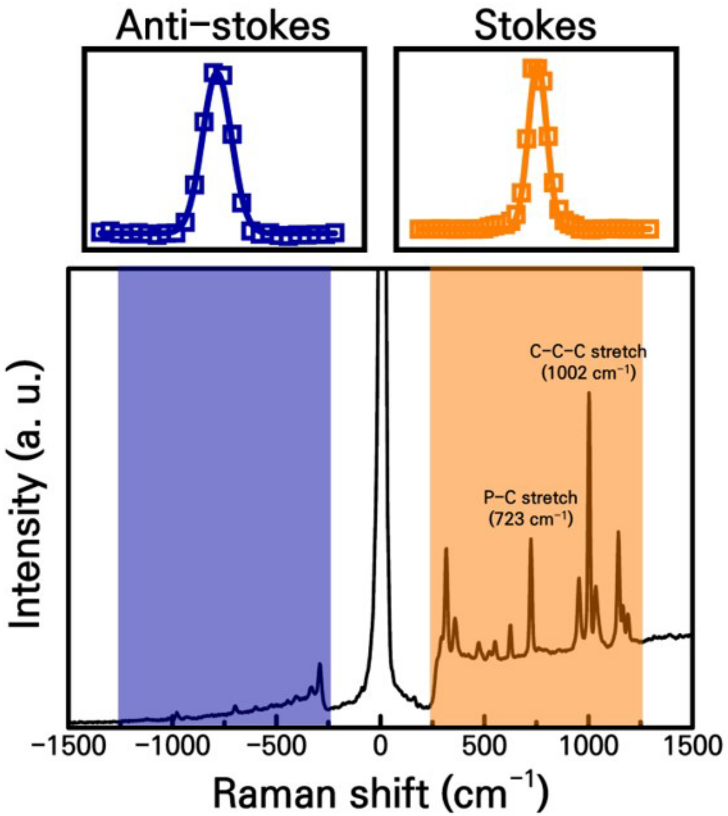
Activation barrier to diffusion of CO: ~0.2 eV

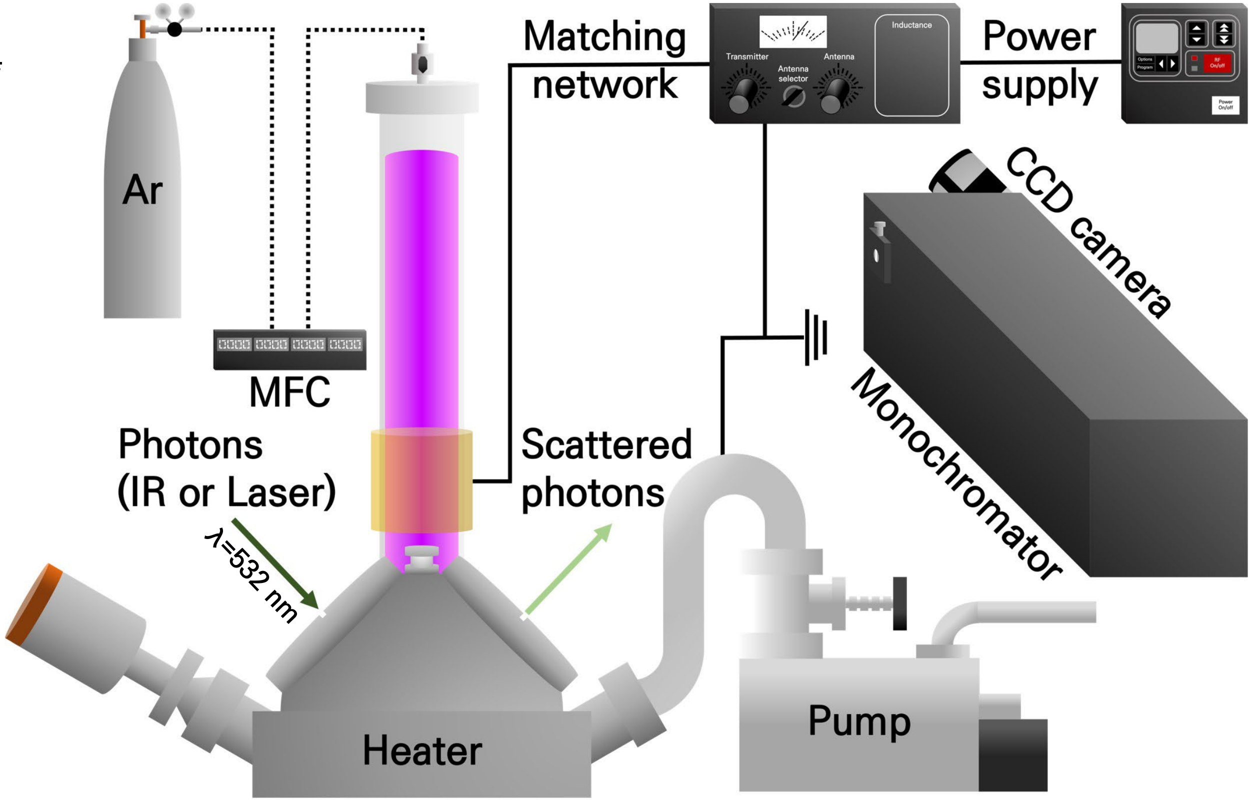
2-1. Raman thermometry

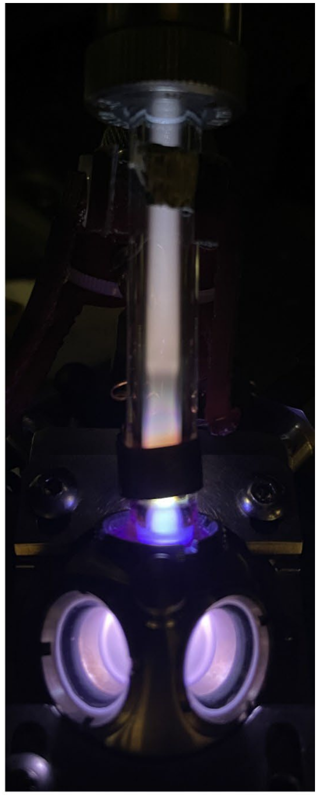
2-1-1. Temperature-dependent population of vibrational mode



$$\frac{I_S}{I_{AS}} = \left(\frac{\lambda_S}{\lambda_{AS}}\right)^4 \cdot e^{-\frac{hv}{KT}}$$





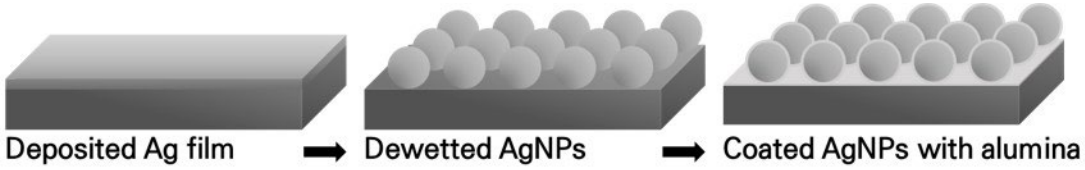


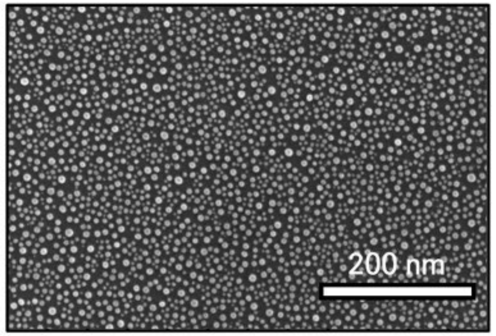
Experimental setup

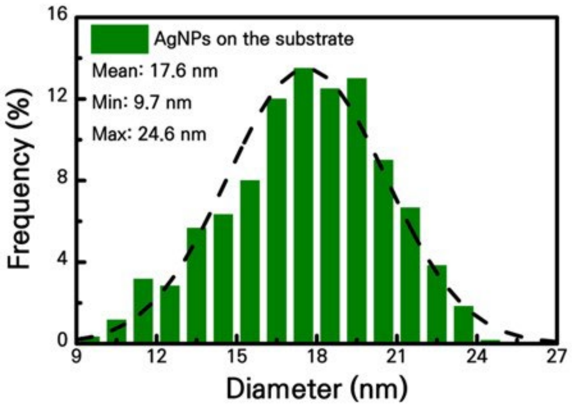
One of the biggest challenge: Too weak signal for Anti-stokes

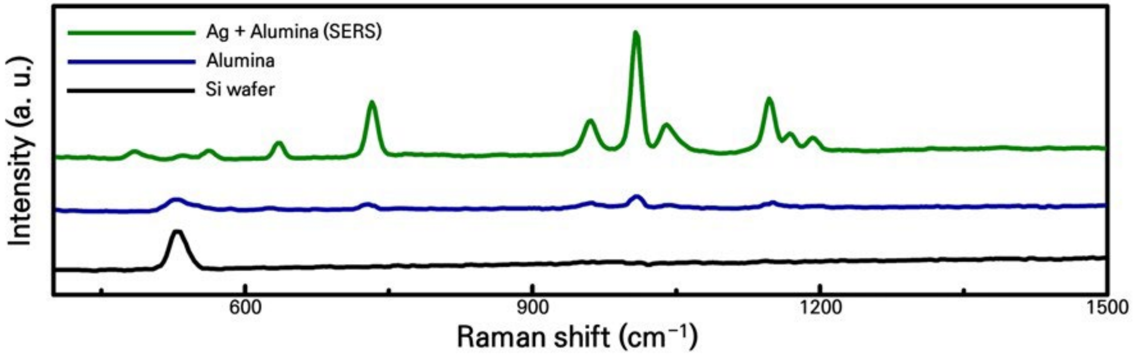
2-1. Raman thermometry

2-1-2. Surface Enhanced Raman Spectroscopy (SERS)

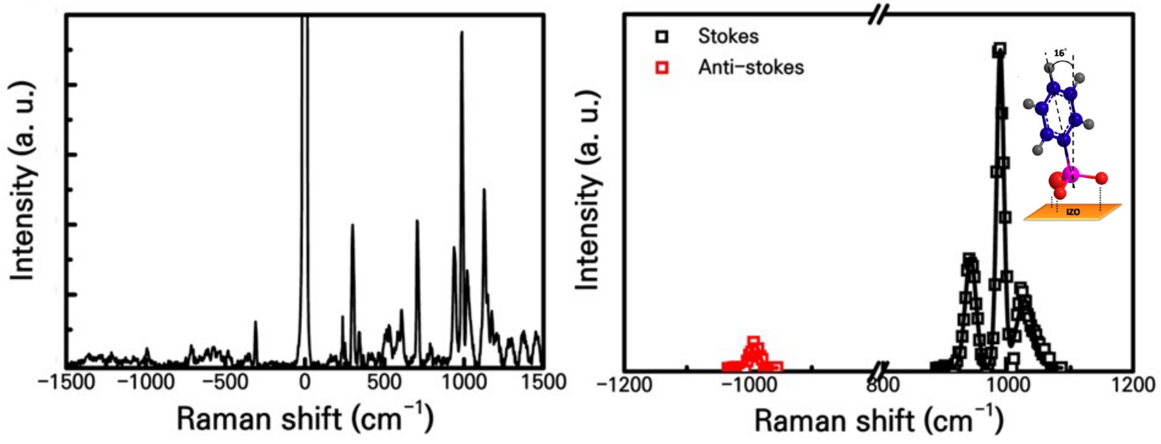








Raman with the argon plasma exposure

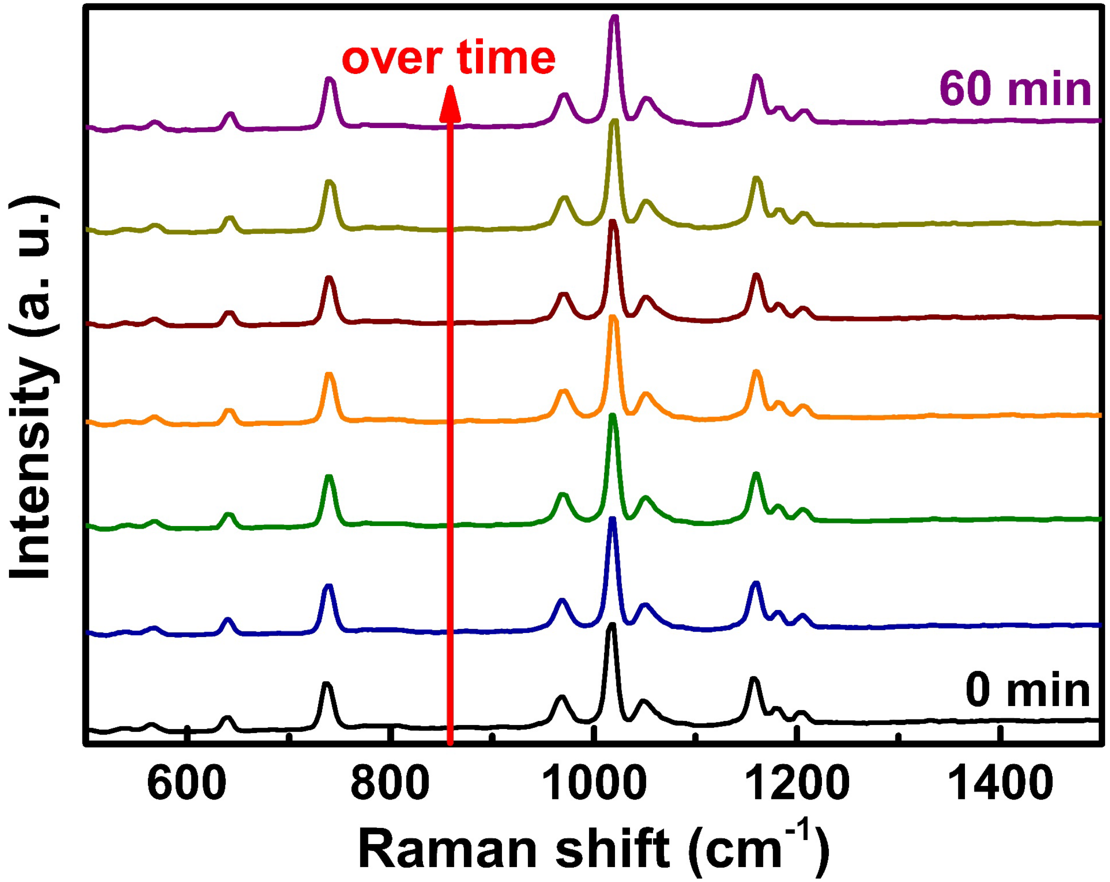


Experimental conditions

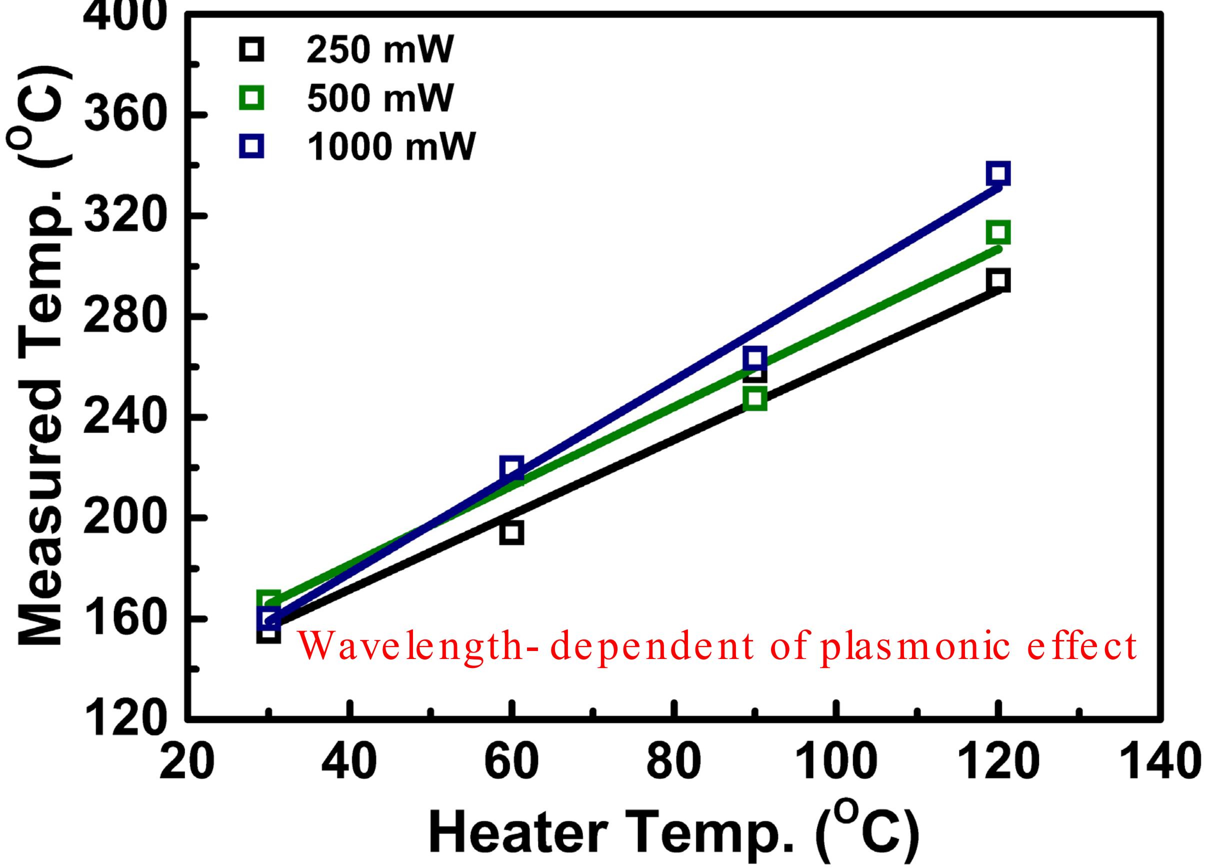
Flow rate of Ar [sccm]	20
Pressure [torr]	3.7
Set temperature [°C]	30, 45, and 60
RF input power [W]	3, 5, and 7

*Actual RF input power was measured through phase difference method.

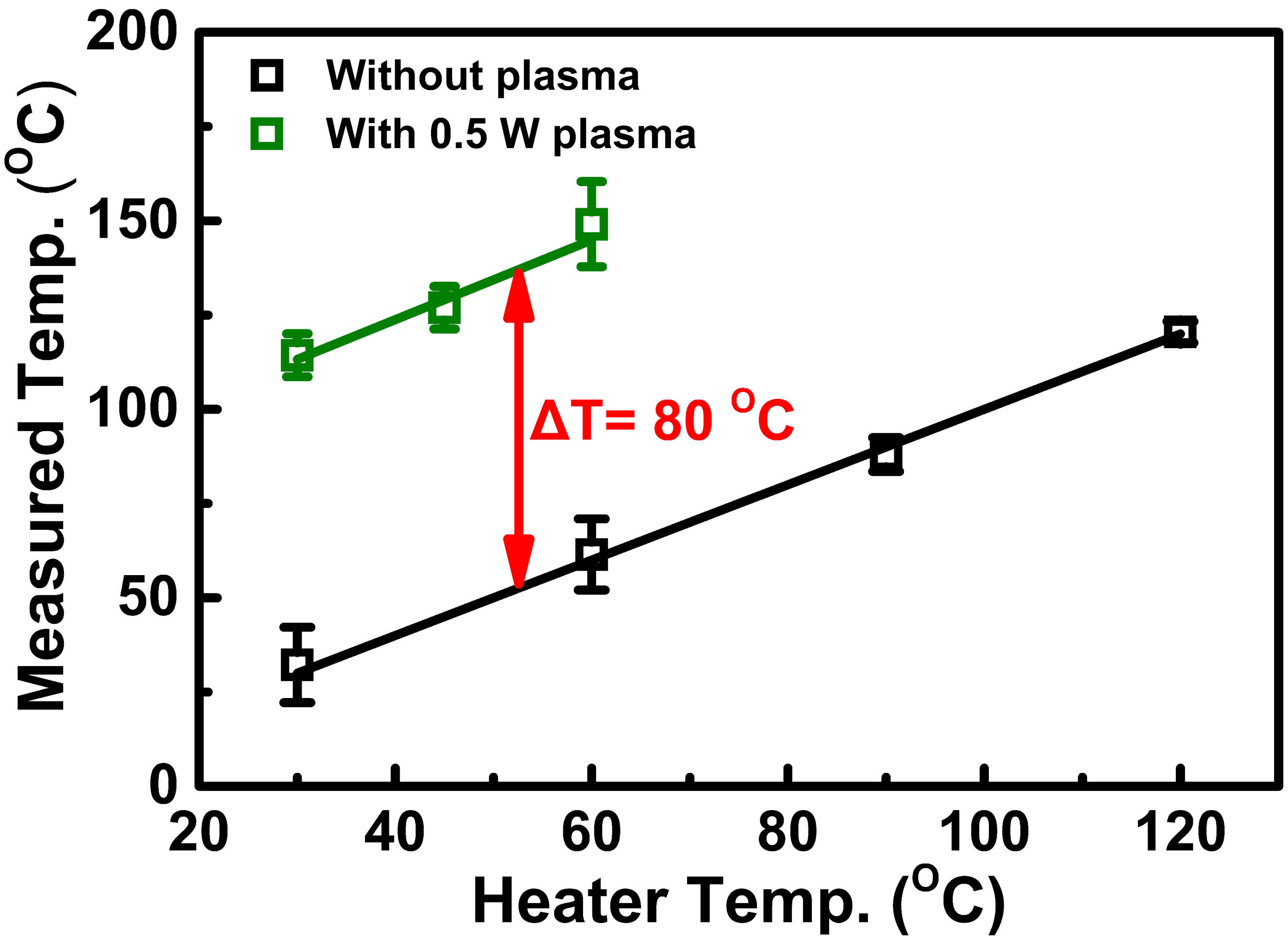
3-1. Raman measurements with PPA



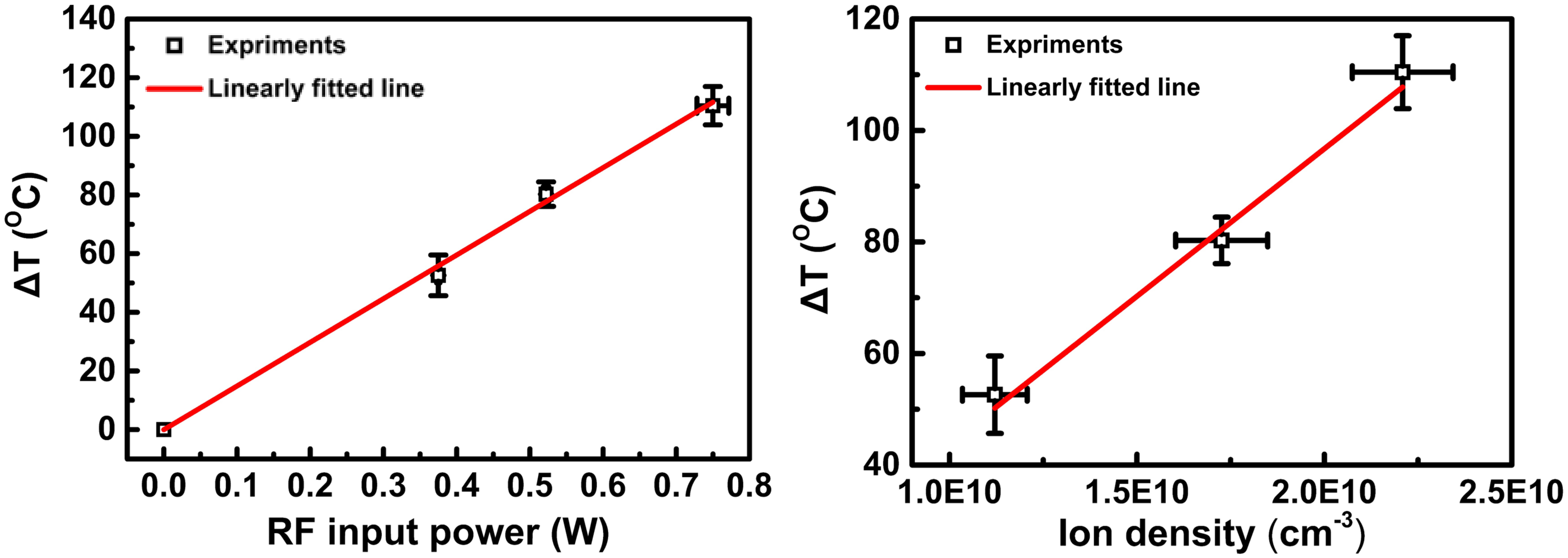
Without plasma exposure



3-2. Measured temperature of PPA with argon plasma exposure



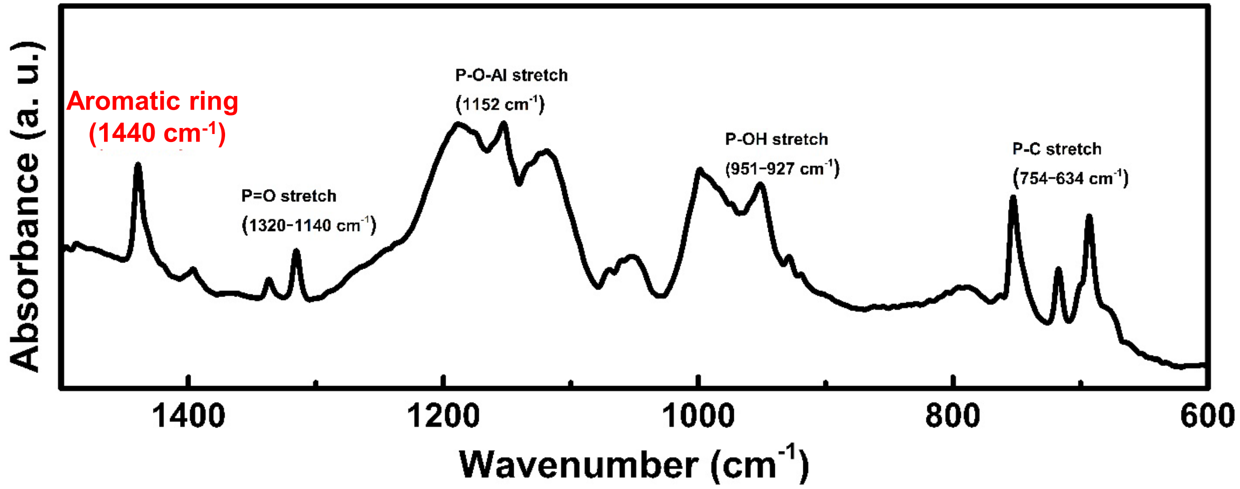
3-2. Measured temperature of PPA with argon plasma exposure

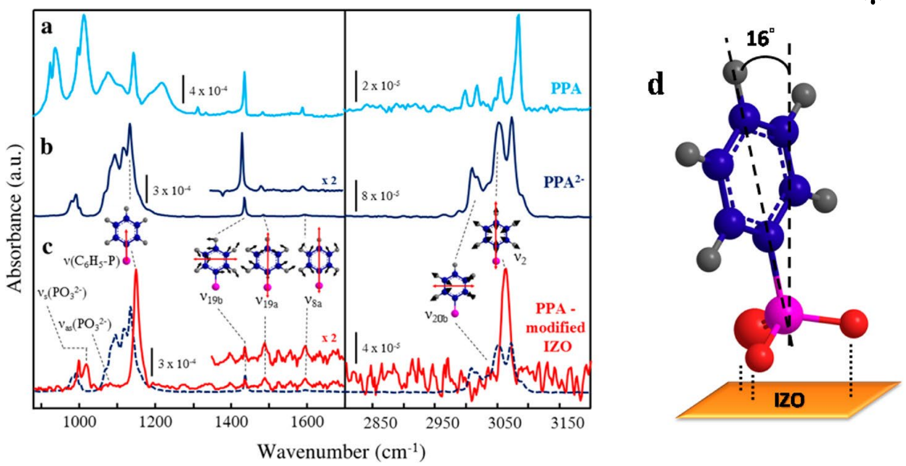


* M. Gliboff et al. *Langmuir*, 29, 2166–2174 (2013).

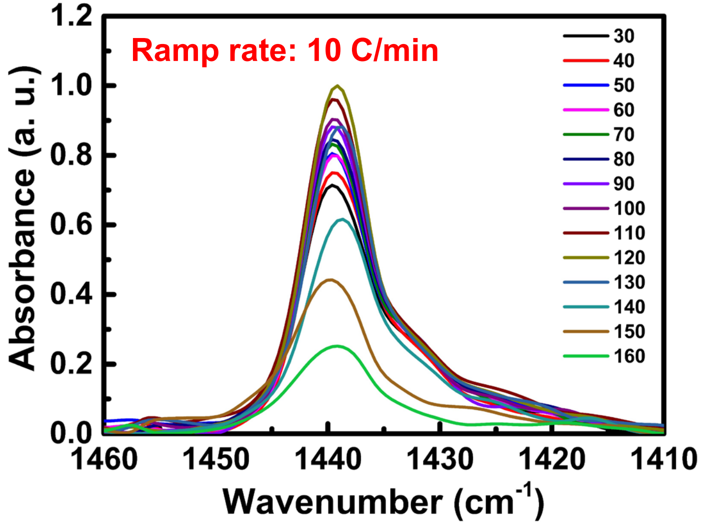
3-3. Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS)

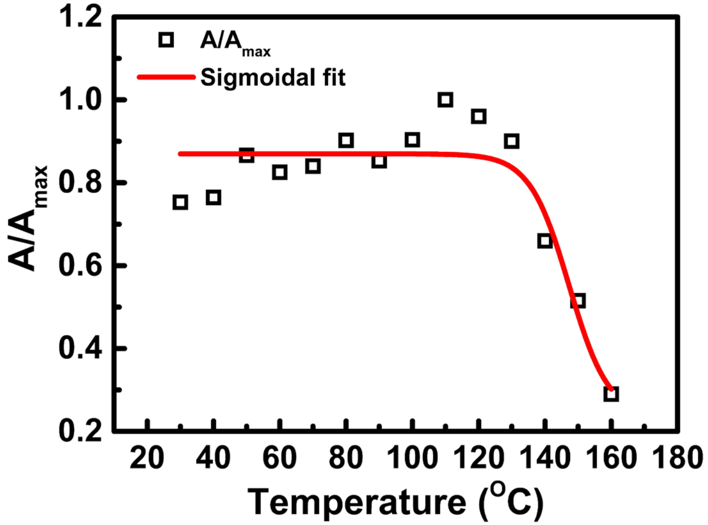
3-3-1. Temperature at the highest desorption

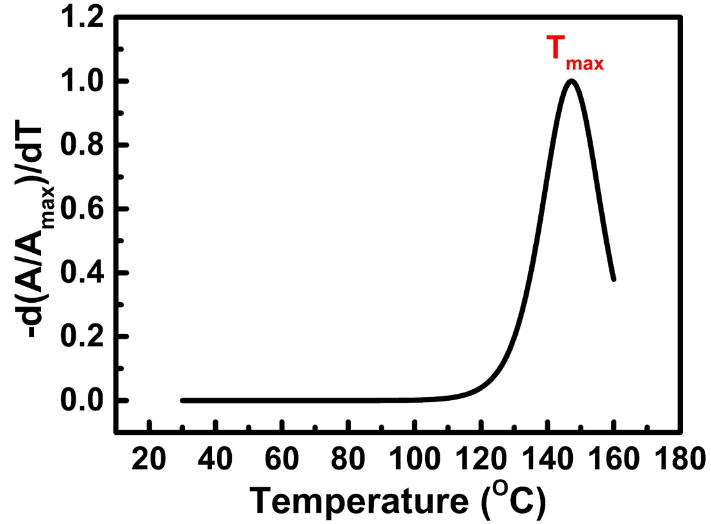




*

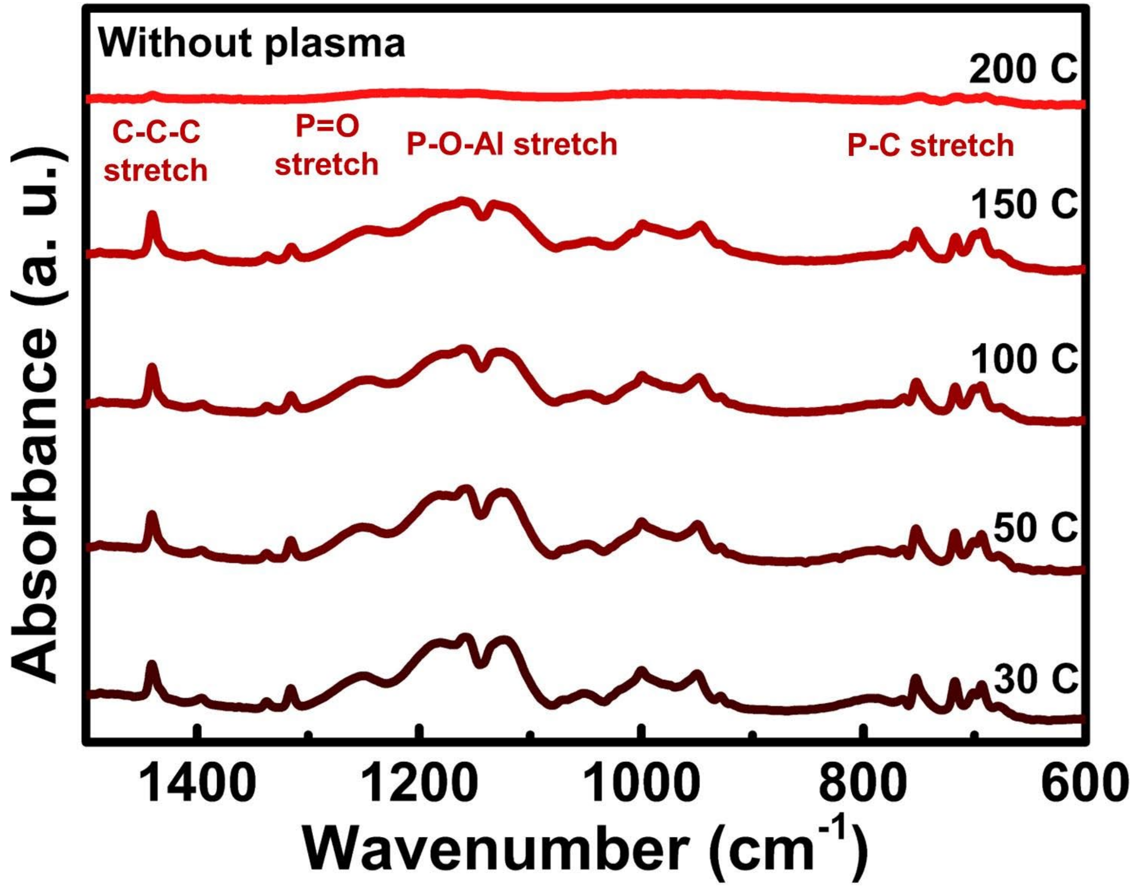


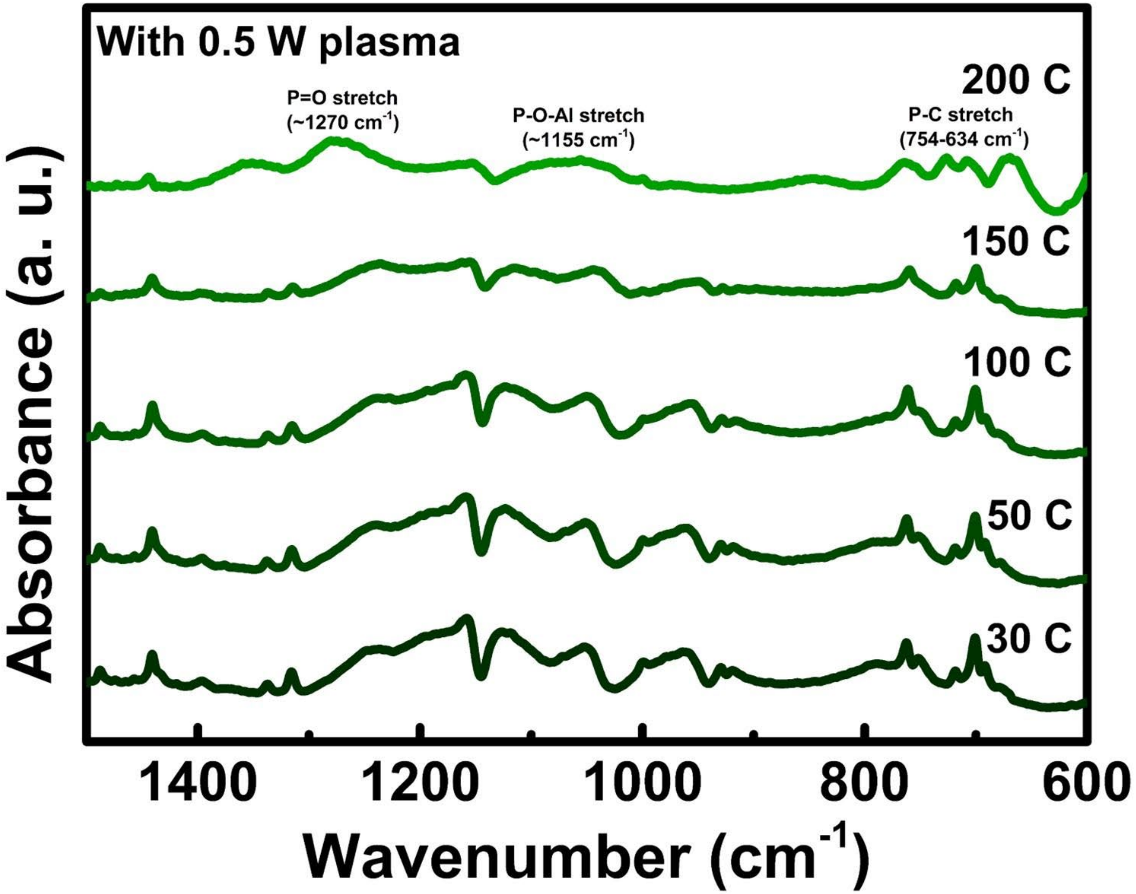




3-3. Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS)

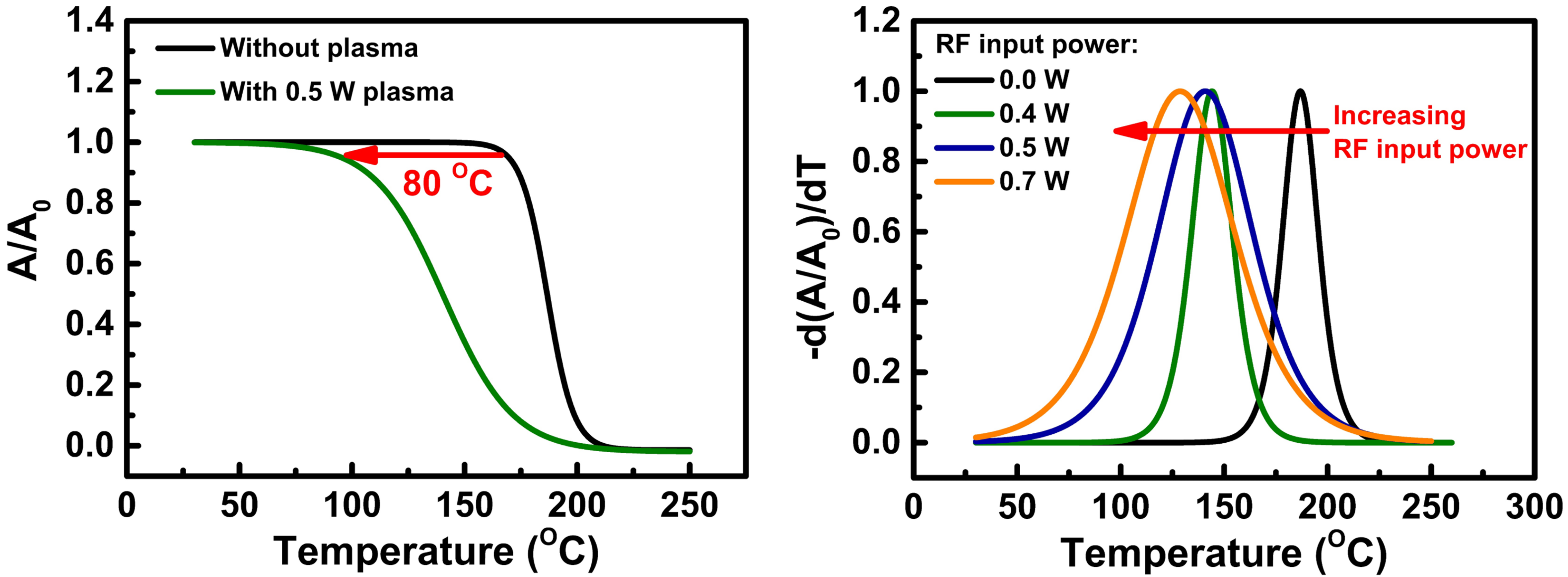
3-3-2. Temperature-dependent DRIFTS measurements





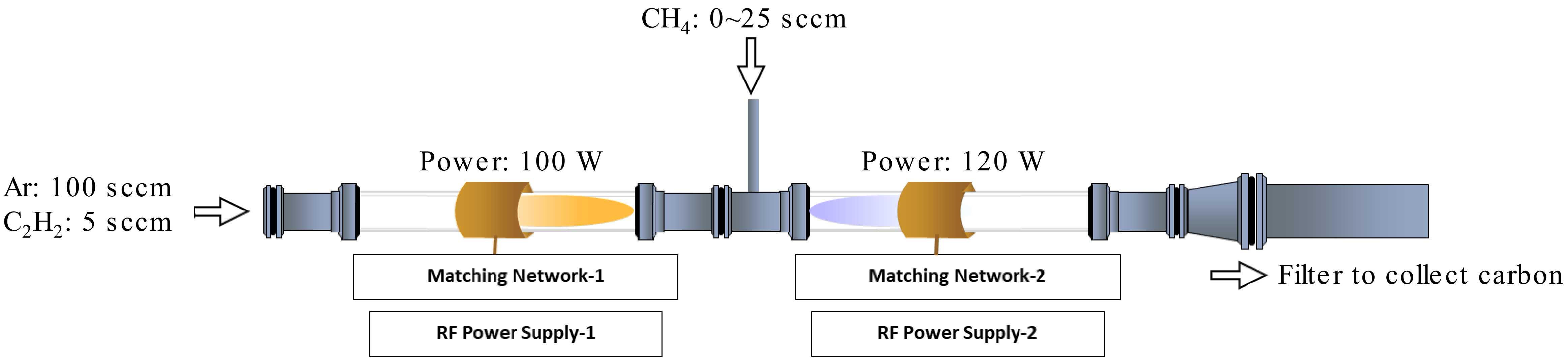
3-3. Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS)

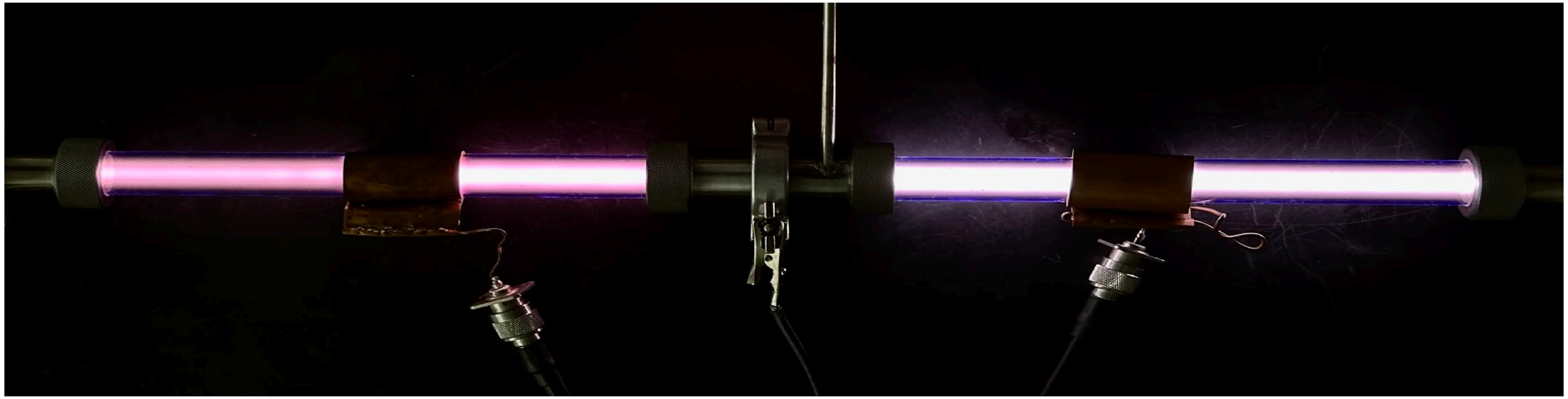
3-3-2. Temperature-dependent DRIFTS measurements



2-1. Experimental details for methane fixation

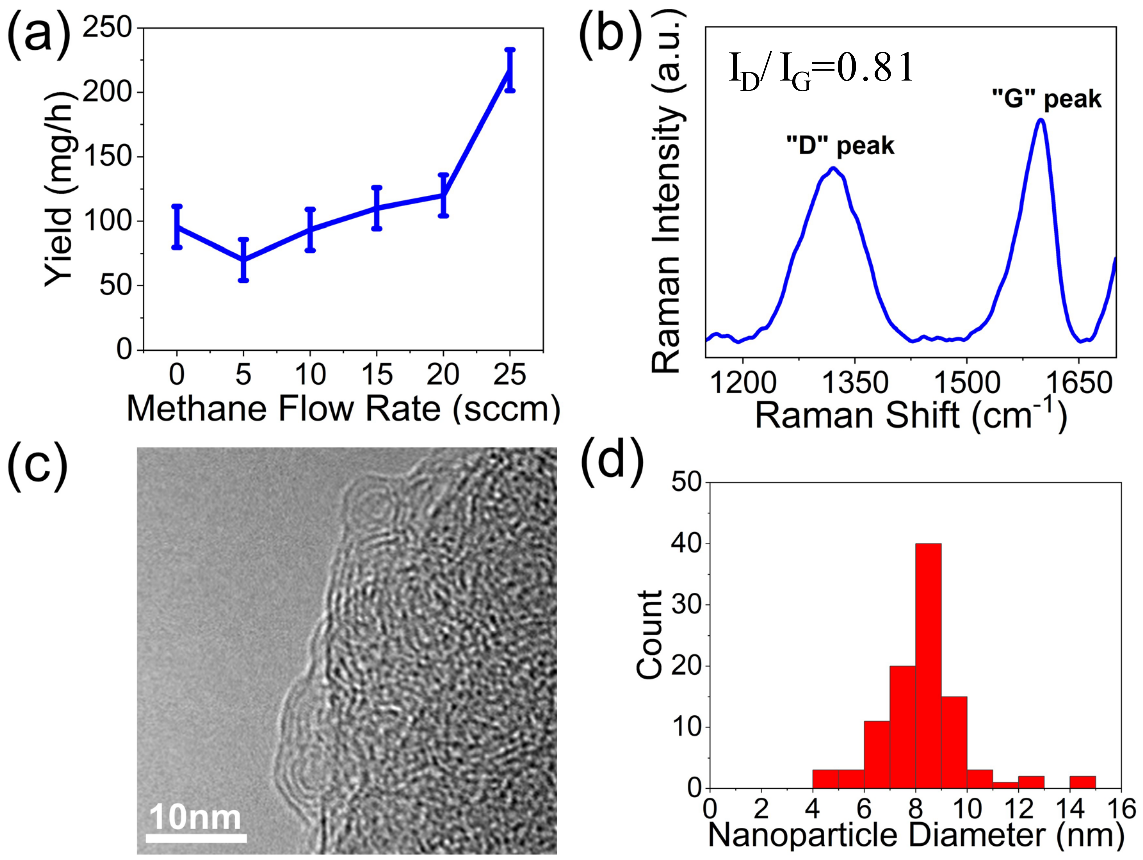
2-1-1. Methane fixation using two-step plasma reactor



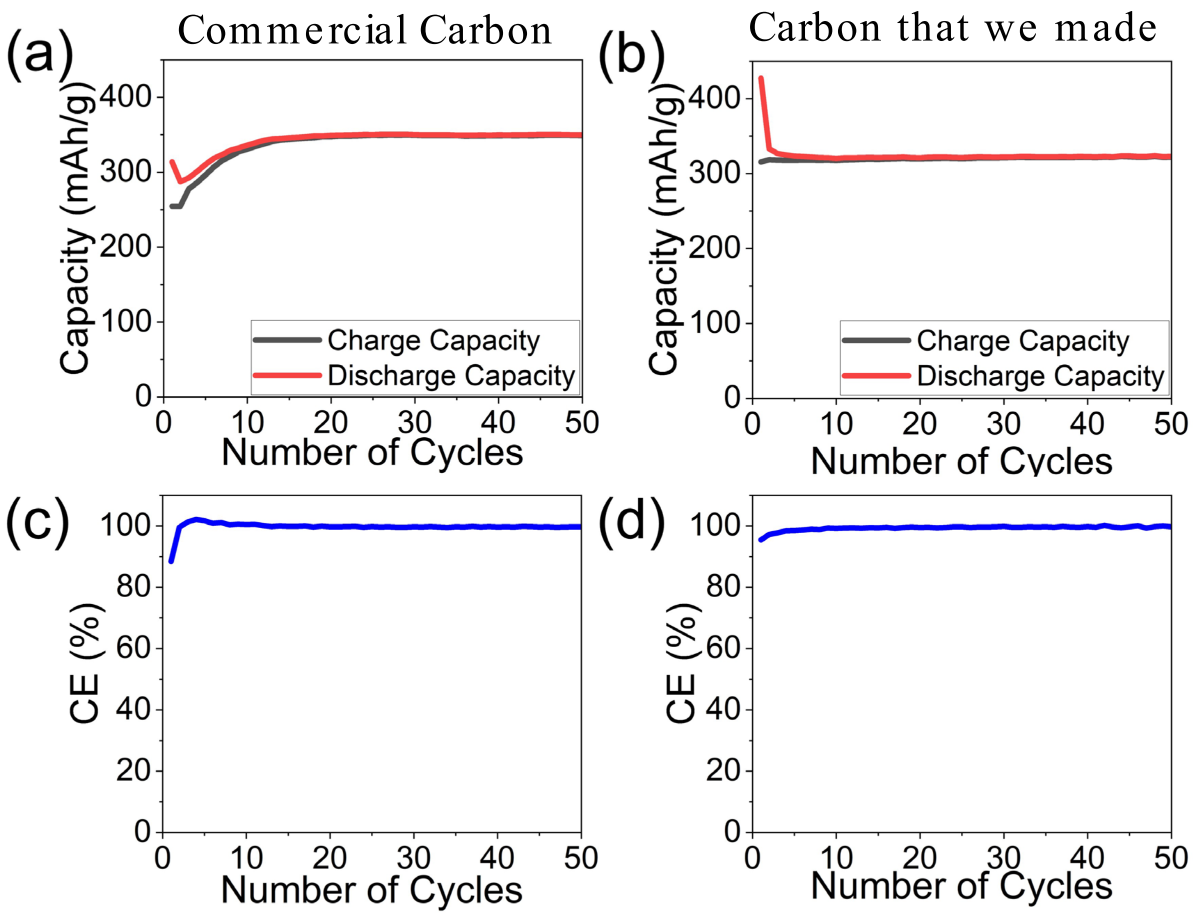


3-1. Results for methane fixation

3-1-1. Characterization of the produced Carbon



3-1-2. Lithium-Ion Battery test



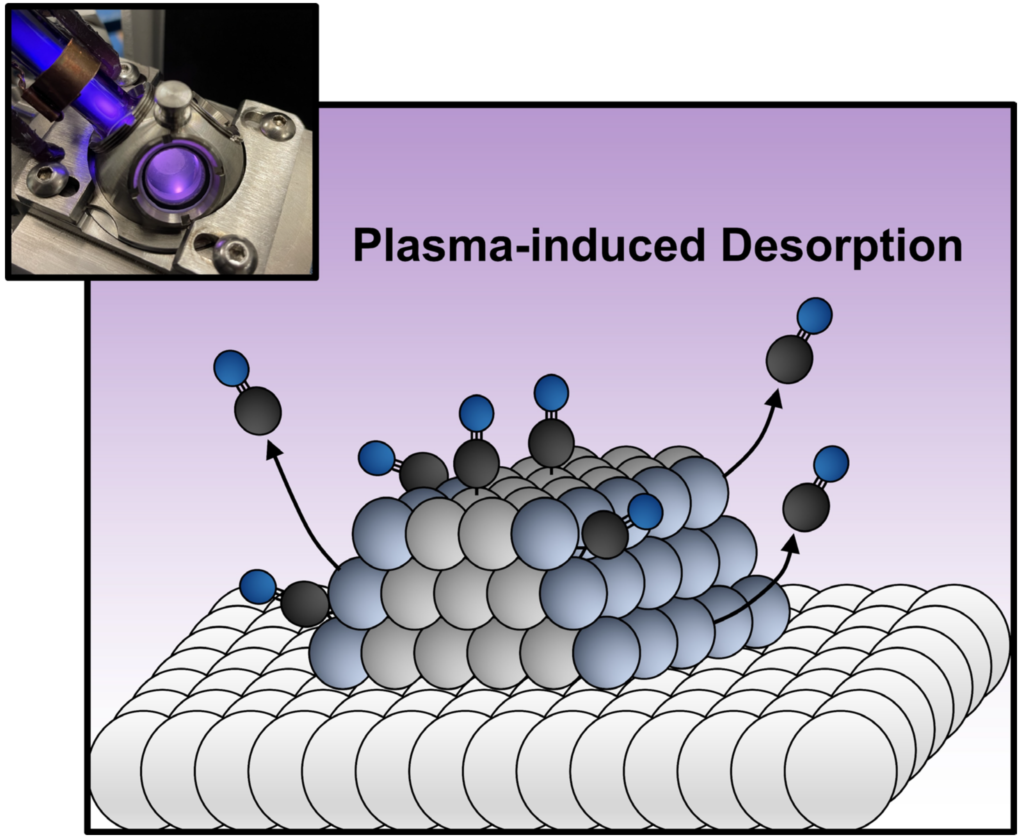
3-1. Results for methane fixation

3-1-3. Comparison with other works

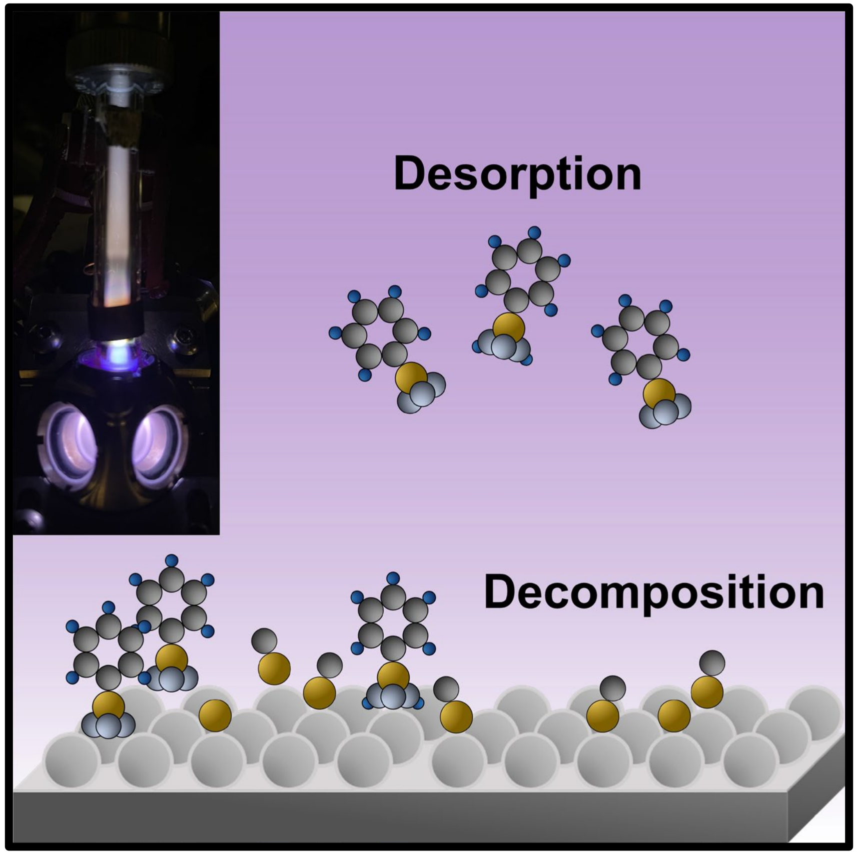
Method	Size of NPs (nm)	I_D/I_G	Type of nano structures	Energy Cost (kWh/g)
Microwave plasma	50-200	0.2-0.3	Particles	□3.7
Microwave plasma	-	0.4-0.5	Sheet-like Carbon	□2.1
Radio-frequency plasma	50-100	0.3-0.4	Flakes	□2.5
Radio-frequency plasma	200-500	0.6-0.8	-	□5
Arc plasma	100-150	-	Sheet-like Carbon	□0.5
Arc plasma	□100	0.3-0.5	Flakes	□8
Arc plasma	50-300	0.4-0.5	Flakes	□0.4
Magnetically-stabilized gliding arc discharge	50-200	0.27	Flakes	□0.4
Current work	4-15	0.81	Particles	□0.473

4-1. Conclusions and achievements

Reduced CO binding energy



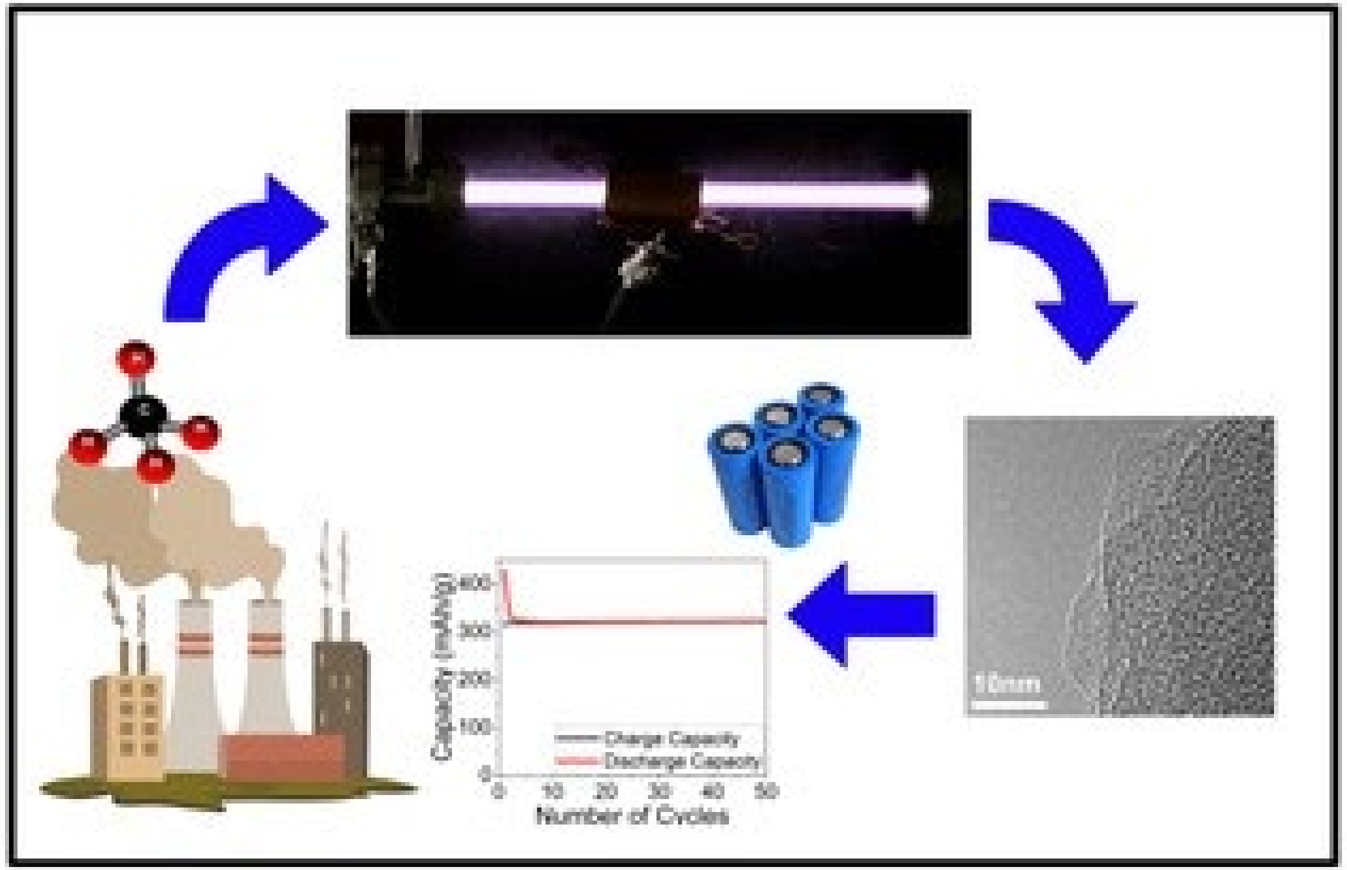
Desorption and decomposition of PPA



*Minseok Kim *et al.* Nonthermal Plasma Activation of Adsorbates: the Case of CO on Pt, *JACS Au*, Under Review.
*Minseok Kim *et al.* Using Surface-Enhanced Raman Spectroscopy to Probe Surface-Localized Nonthermal Plasma Activation, *J. Phys. Chem. Lett.* **2024**, *15*, 4136-4141.
*Minseok Kim *et al.* Combining in operando FTIR and Raman to investigate the plasma-surface interaction, *The 76th Annual Gaseous Electronics Conference*, 2023.

4-1. Conclusions and achievements

Hydrogen and Carbon production from Methane



*Aishwarya Belamkar *et al.* Energy Efficient Methane Fixation Using a Low-Temperature Dusty Plasma, *ACS Appl. Nano. Mater.* Under Review.
*Aishwarya Belamkar *et al.* Synthesis of Carbon Nanoparticles from Methane Using a Non-Thermal Plasma, *The 76th Annual Gaseous Electronics Conference*, 2023

4-2. Acknowledgements

U.S. Department of Energy
National Energy Technology Laboratory
Grant No. DEFE0032091

Minseok Kim

PhD student
Email: mkim435@ucr.edu

Lorenzo Mangolini

Principal Investigator
Email: lmangolini@engr.ucr.edu