Graphene-based Electrodes for Electrochemical Energy Conversion

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AVS North California Chapter

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Graphene for electrochemical devices

Properties

- Electron conducting
- High surface area
- Catalytic

Applications

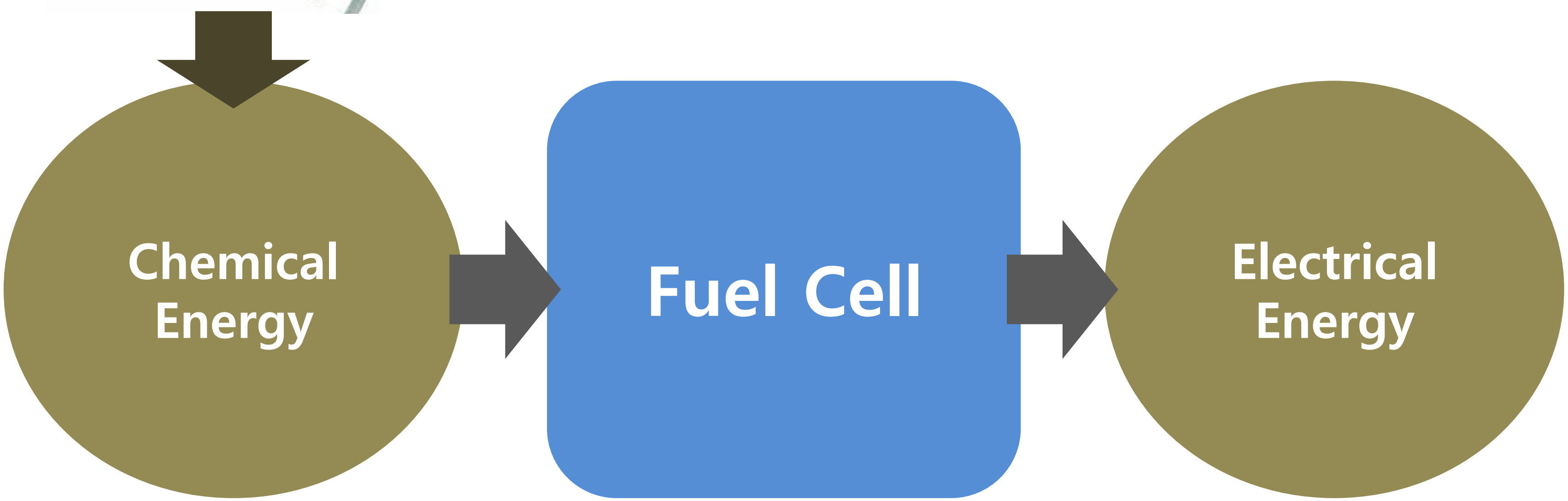
- Batteries
- Supercapacitors
- Fuel Cells
- Sensors
- …

What is a fuel cell?

Electrochemical “Energy Conversion” Device

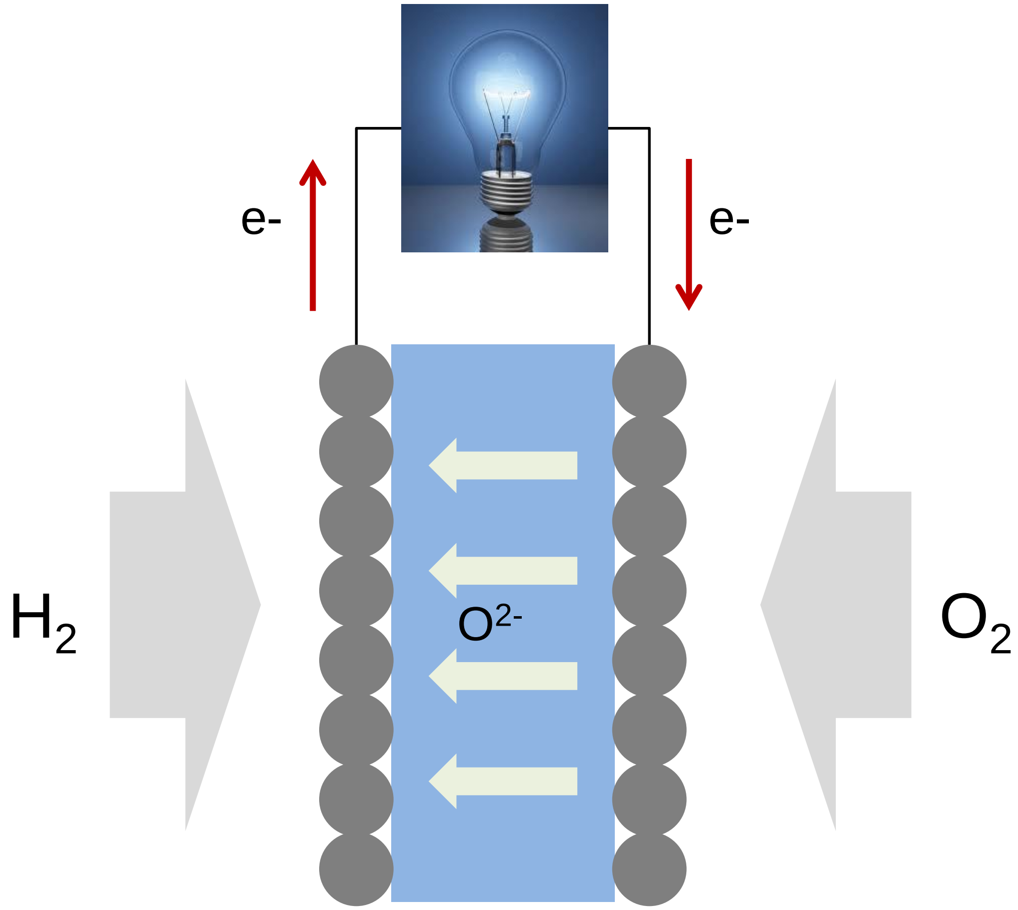
Fuel

: **hydrogen,** alcohols, hydrocarbons, etc.



Efficient and quiet

Fuel cell operation

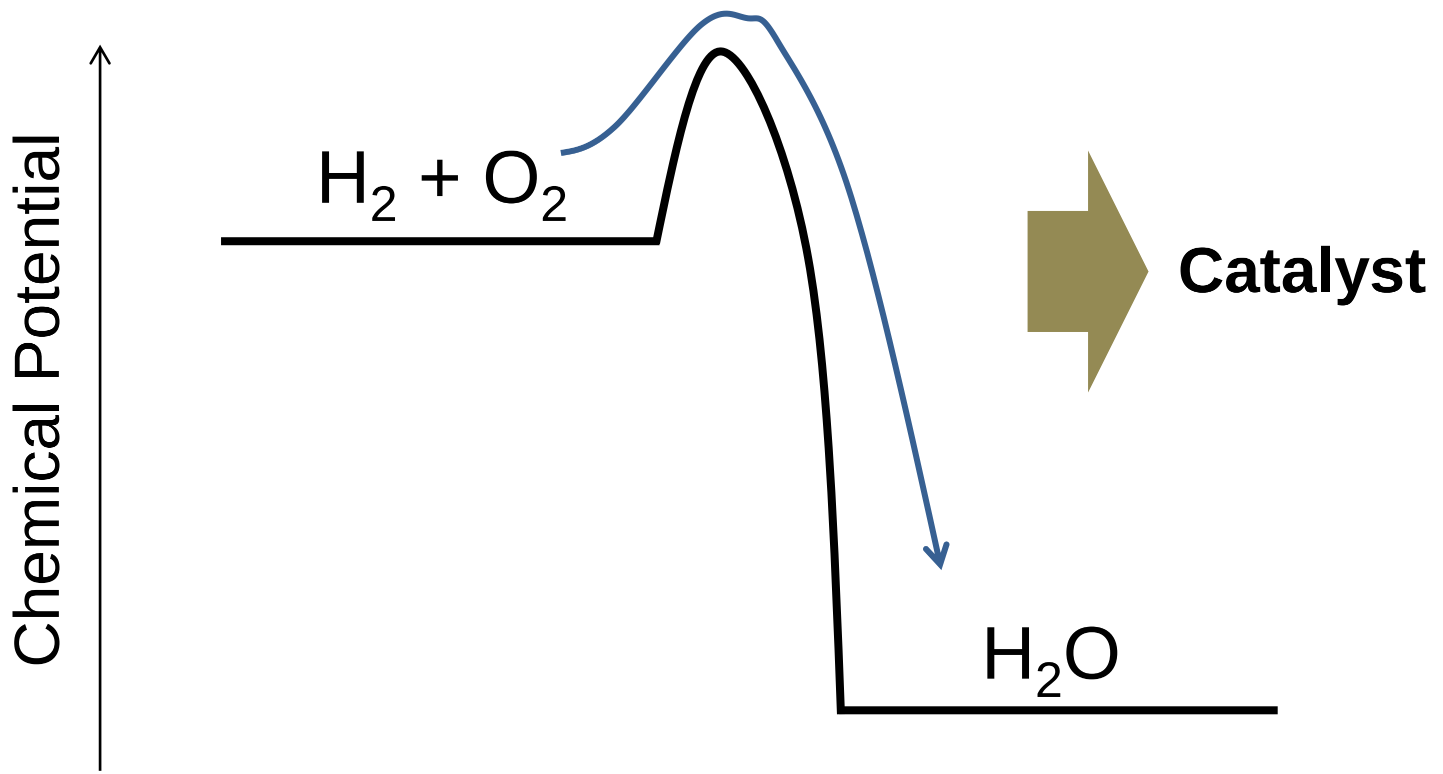


$$H_2 \rightarrow 2H^+ + 2e^- \ (\textbf{HOR}) \qquad \tfrac{1}{2}\, O_2 + 2e^- \rightarrow O^{2-} \ (\textbf{ORR})$$

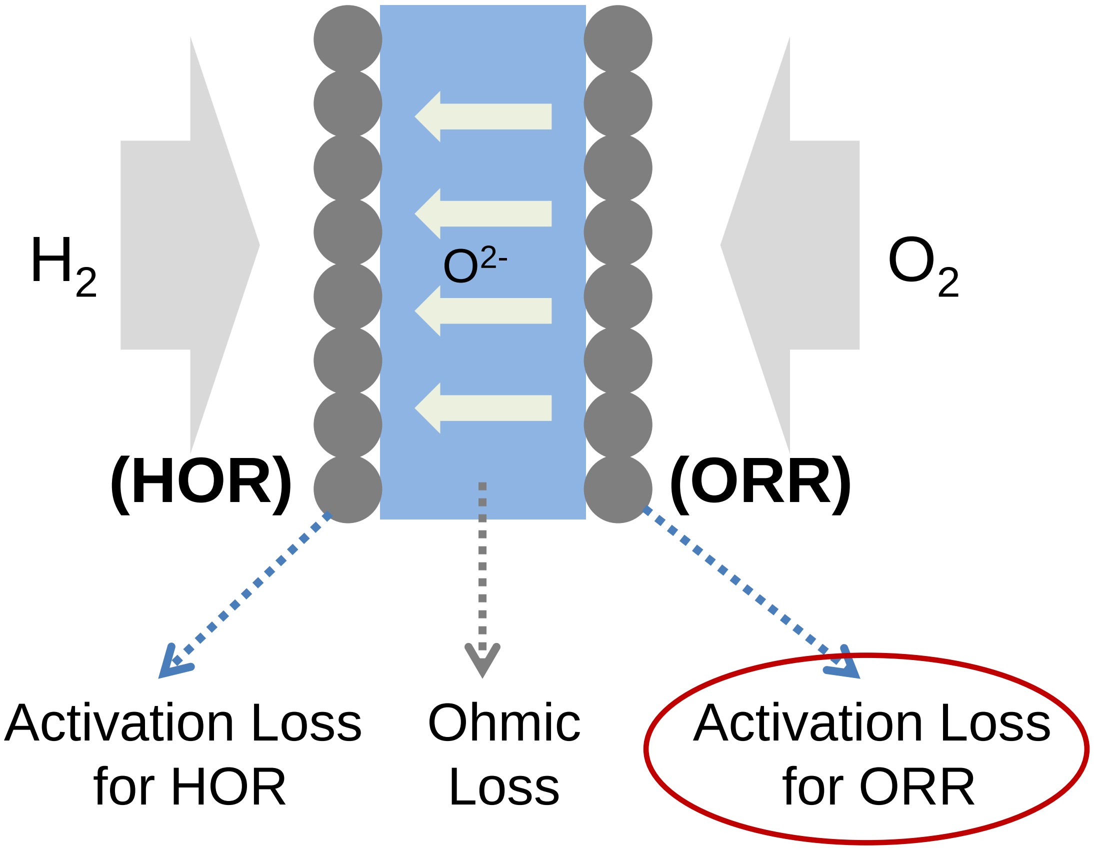
Overall: $H_2 + \tfrac{1}{2}\, O_2 \rightarrow H_2O + \text{electricity}$

Driving force?

Ans. The chemical potential difference between the reactants ($H_2 + O_2$) and the product (H_2O)



Cell losses



H_2
O^{2-}
O_2
(HOR)
(ORR)
Activation Loss for HOR
Ohmic Loss
Activation Loss for ORR

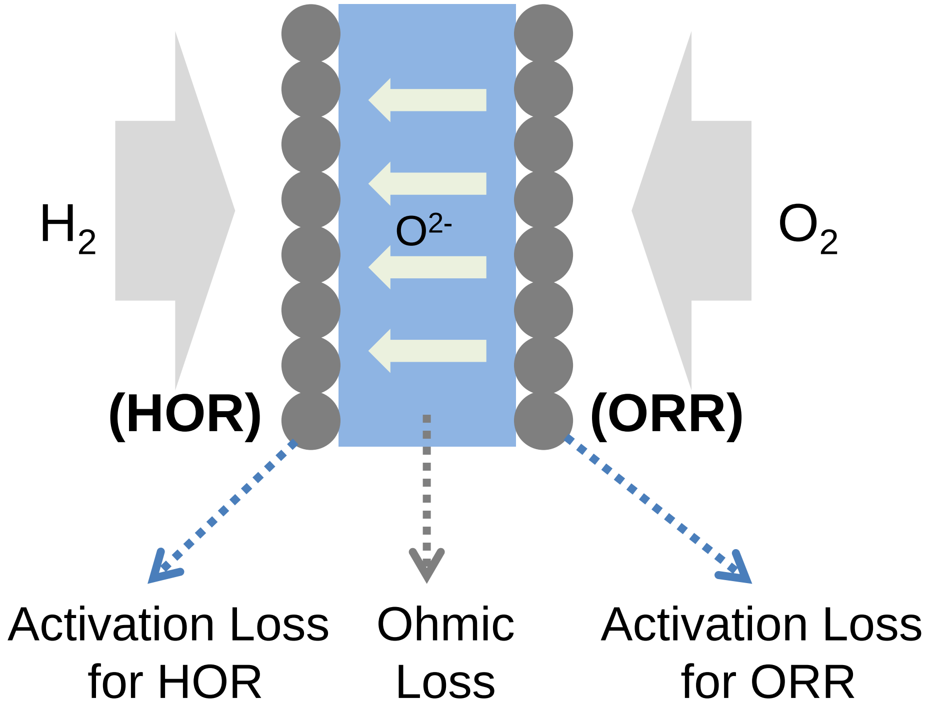
Solid Oxide Fuel Cell (SOFC)

High Operating Temperature
> 800 °C

- Advantages
  - →Fuel Flexibility
  - →Simpler System (No humidity control, etc.)
- Disadvantages
  - →Material/Part selection
  - →Durability
  - →Limited applicability

Lower Operating Temperature!
(< 400 ℃)

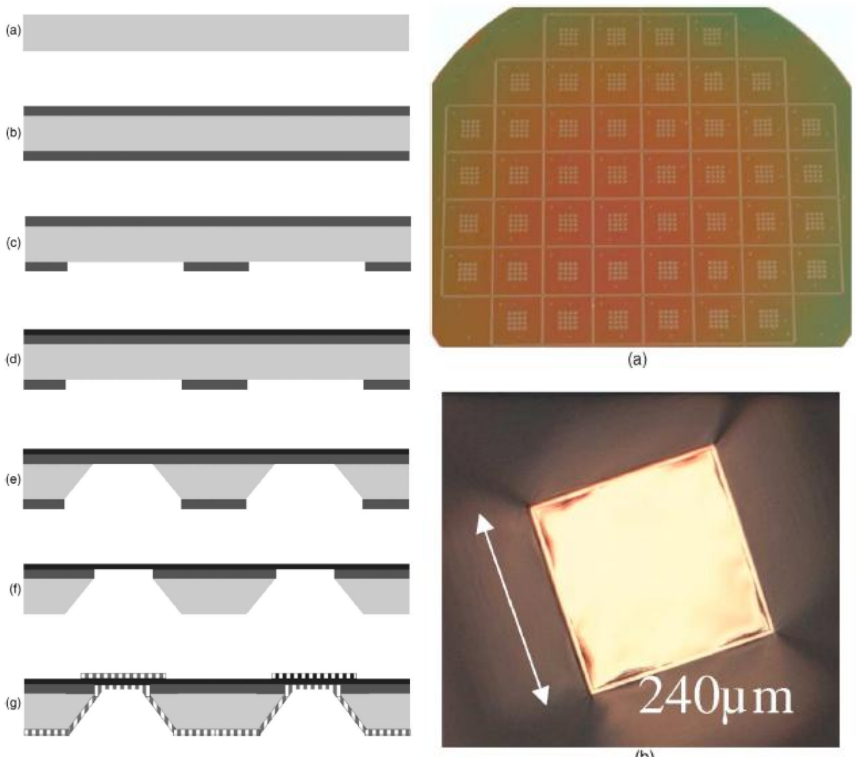
Reduction in T causes significant Losses!



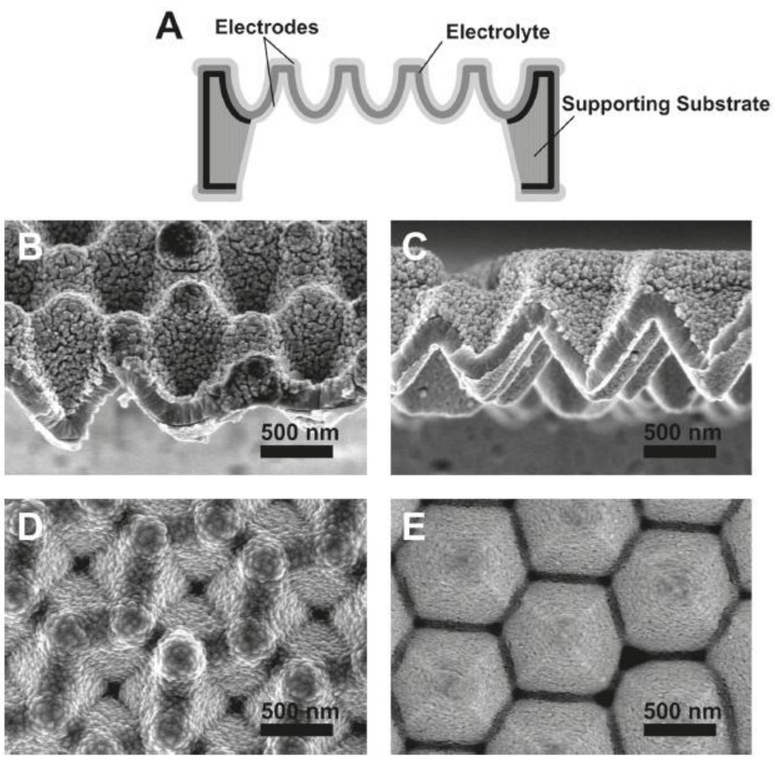
Both ohmic and activation loss $\propto$ ***exp(E$_a$/kT)***

To counteract the significant ohmic loss

Thinning the electrolyte < 100 nm



H. Huang et al. J. Electrochem. Soc., 154, B20, 2007



Y. B. Kim et al. Electrochem. Comm., 13, 403, 2011

To counteract the significant electrode loss

Need a totally new material system because…

- Conventional perovskite-based electrodes
  → Not active at low temperatures
- Pt-based electrode
  → Expensive
  → Fast degradation

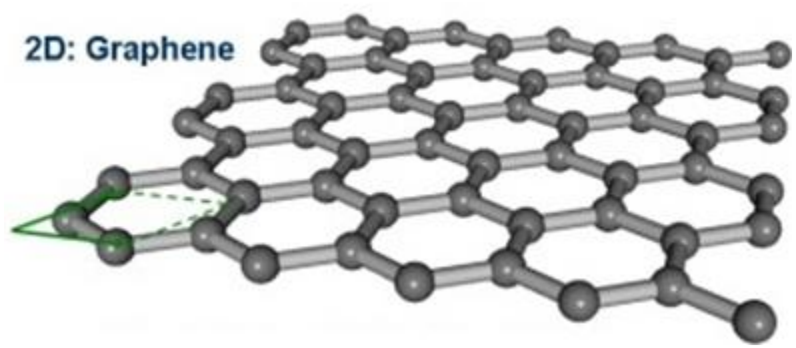
Try doped graphene

New air electrode (cathode) materials for LT-SOFCs

Doped Graphene?

Why graphene as the cathode?

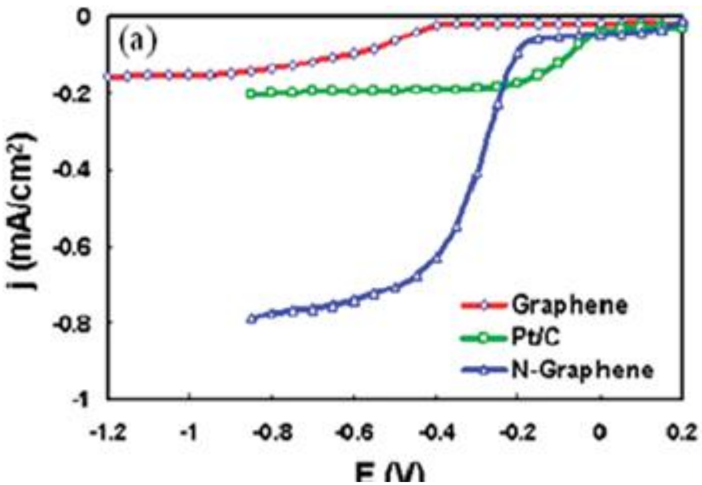
- **Graphene (and its derivatives)**
  - Extraordinary thermal and electrical conductivities
  - High specific surface area (theoretically 2630 m^2/g for single-layer)
  - Strong mechanical strength and flexibility
  - Excellent catalytic activity (Doped Graphene)

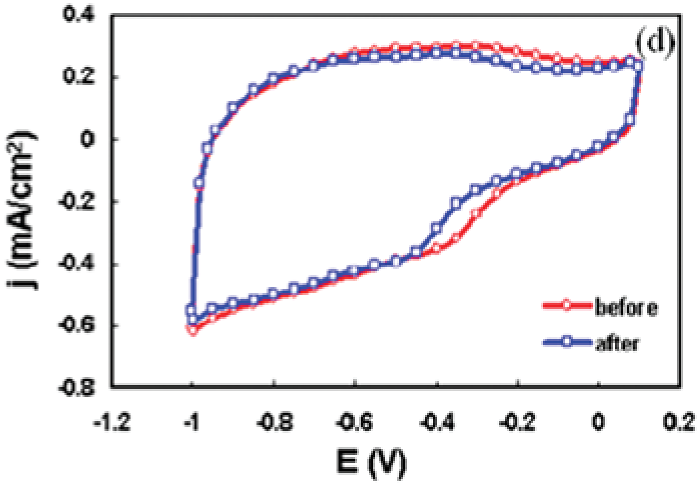


Qu et al. *ACS Nano*, 4, 1321, 2010

N-doped Graphene as an ORR catalyst in Fuel Cell

Catalytic Activity	Durability over cycle (200k cy.)





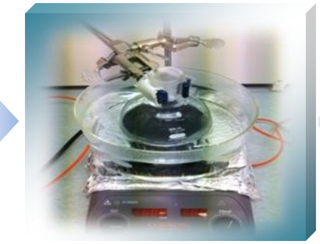
- Catalytically superior to Pt
- Highly durable
- Resistant to CO and methanol poisoning

Qu et al. *ACS Nano*, 4, 1321, 2010

Solution & symmetric cell preparation procedure

GO (Graphene Oxide)

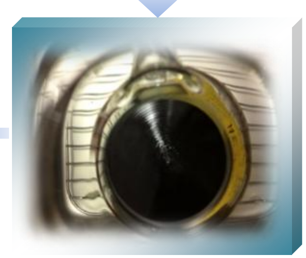
Flake graphite powder



Expansion of graphite sheets

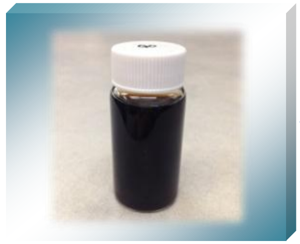
Oxidization using $KMnO_4$

Filtration with PTFE filter



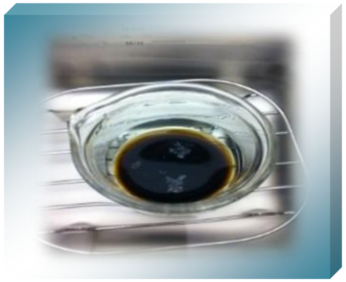
Sonication for better dispersion

Centrifuging to remove unexfoliated particles



Graphene oxide solution

NrGO (Nitrogen Doped Reduced Graphene Oxide)



GO solution
+ dicyandiamide(DCDA)
+ D.I. water

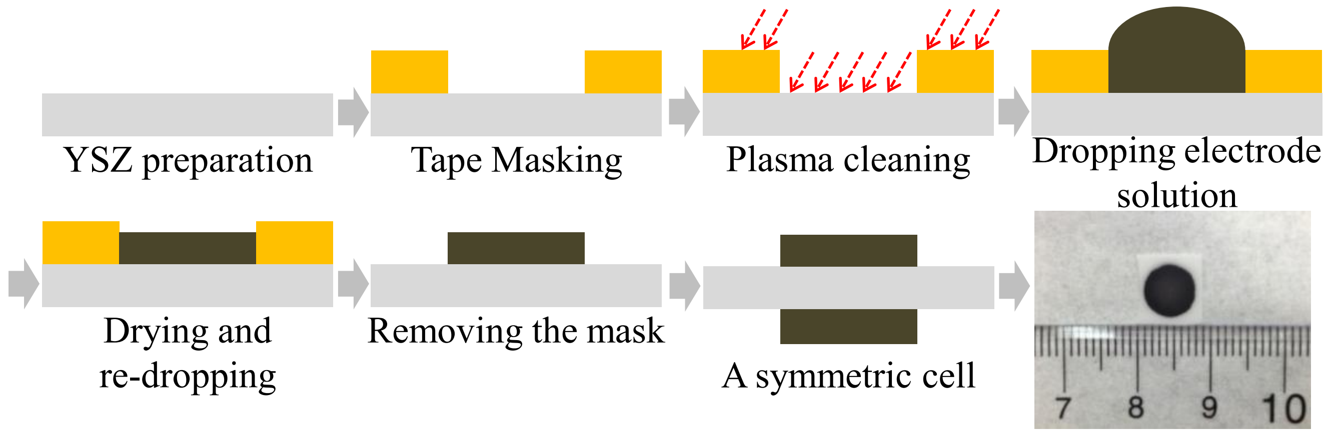
Teflon-lined auto-clave

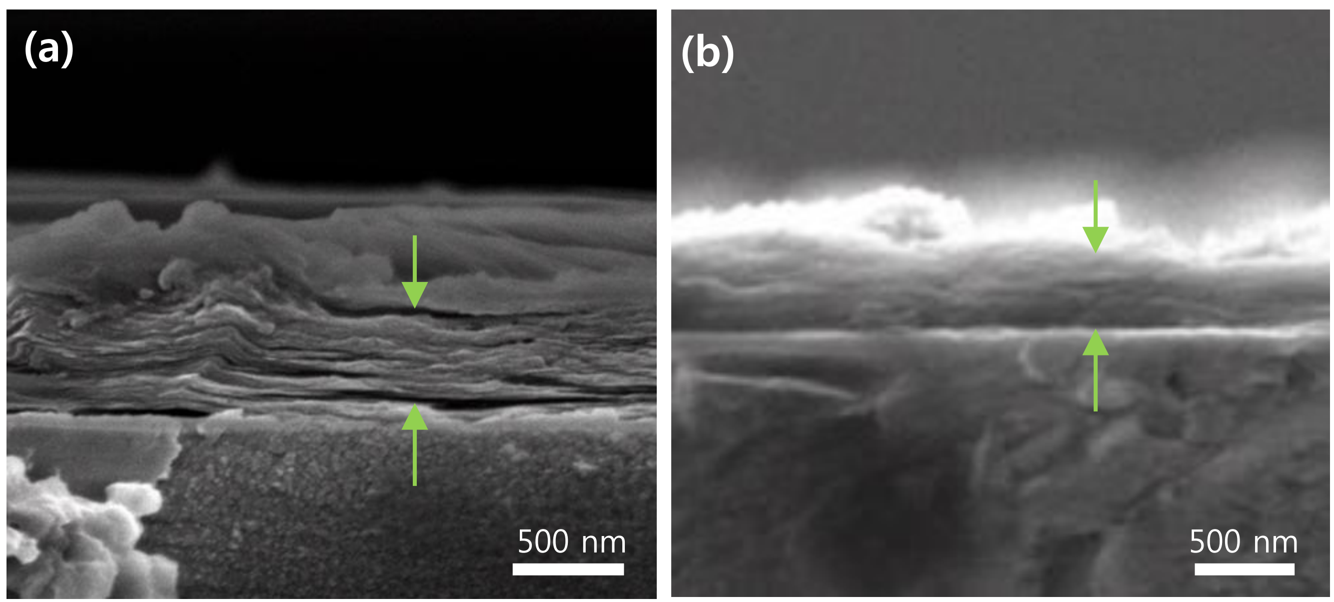
Hydrothermal rxn. @ 140, 180°C

sonication in the suspension (90% water+10% MeOH)

Graphene-based electrode deposition

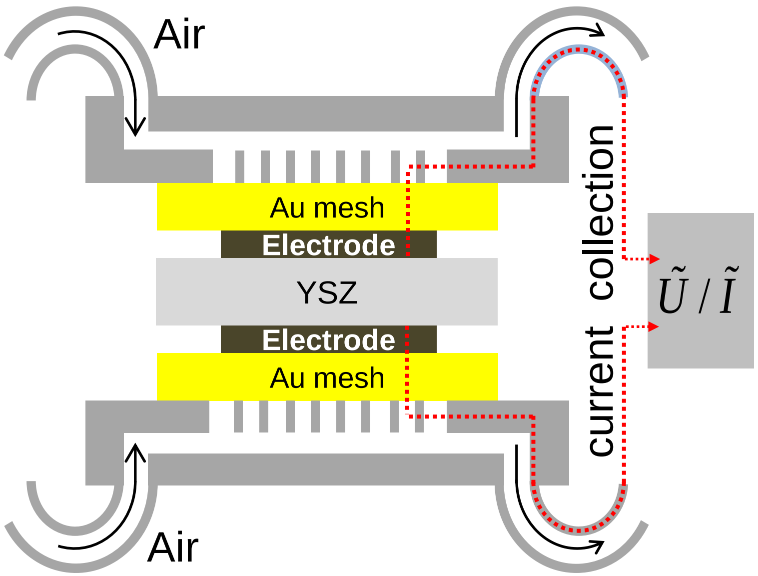
- rGO
- NrGO140
- NrGO180

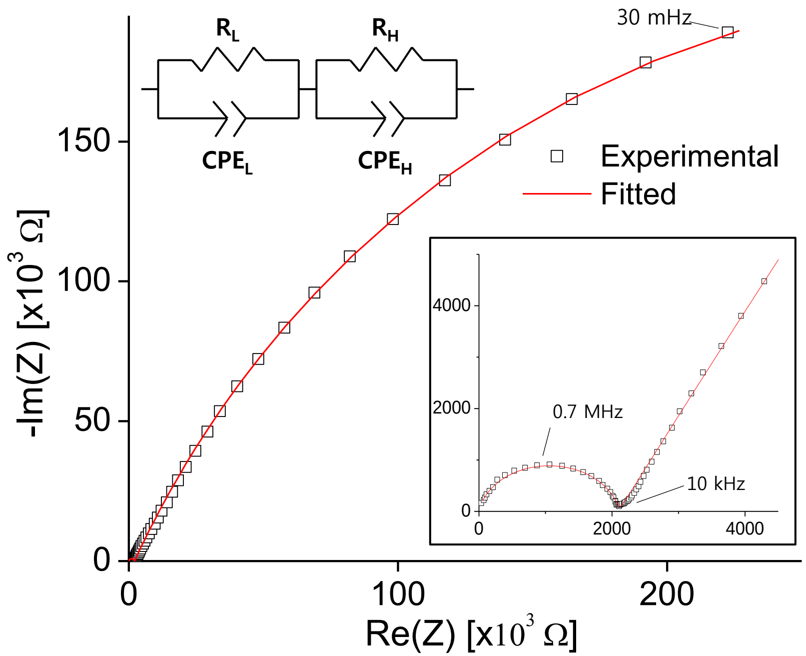




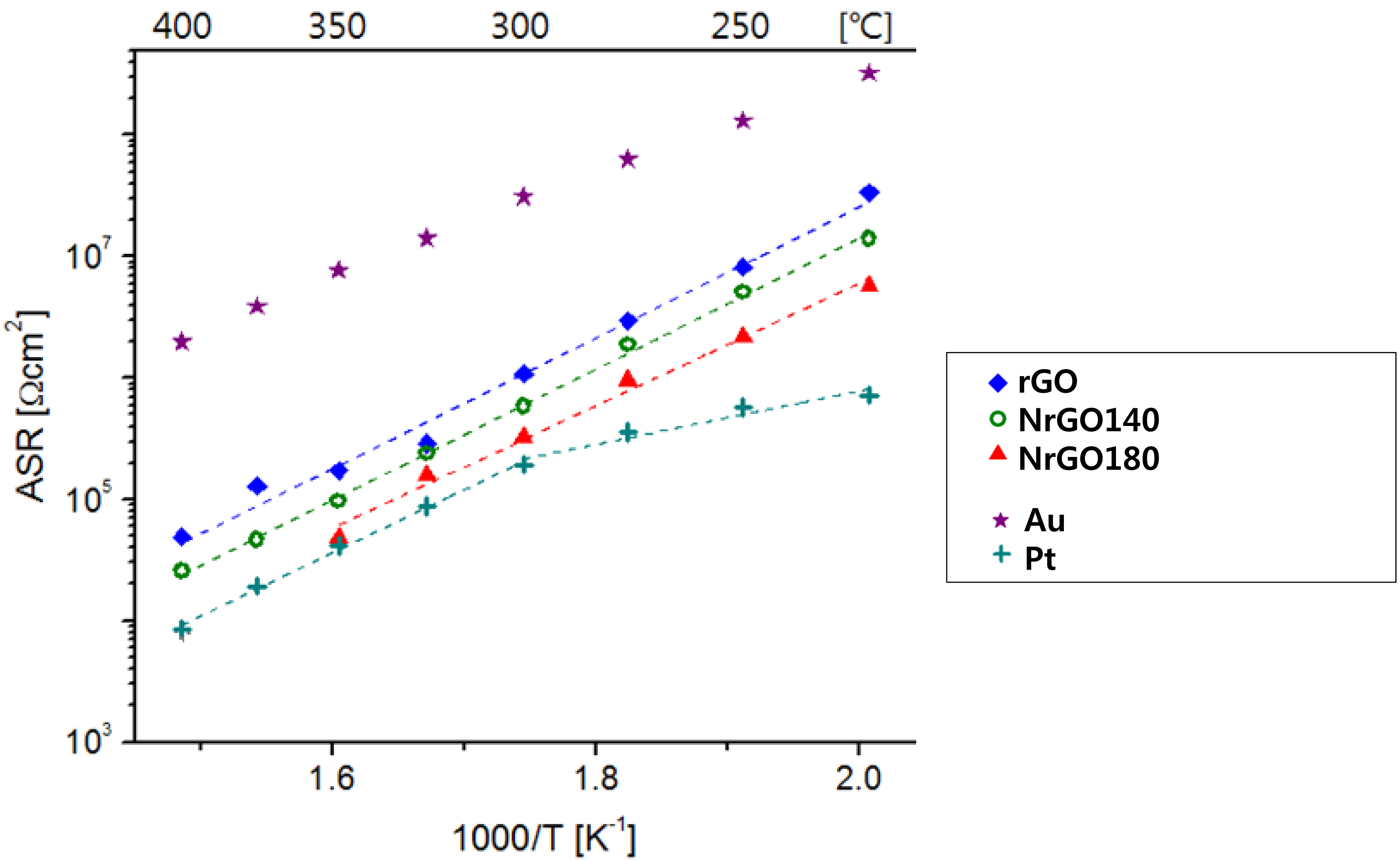
rGO NrGO180

Electrochemical Impedance Meas.



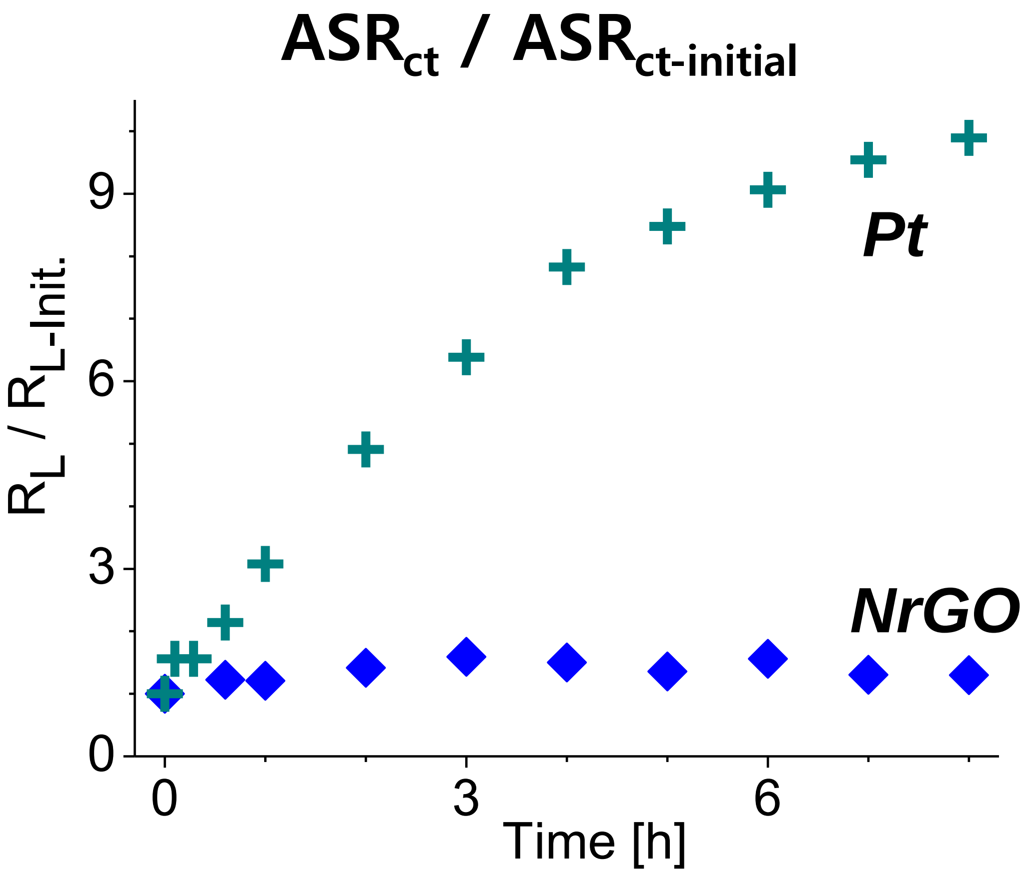


Oxygen Reaction Performance



Y. Jee et al. *submitted*

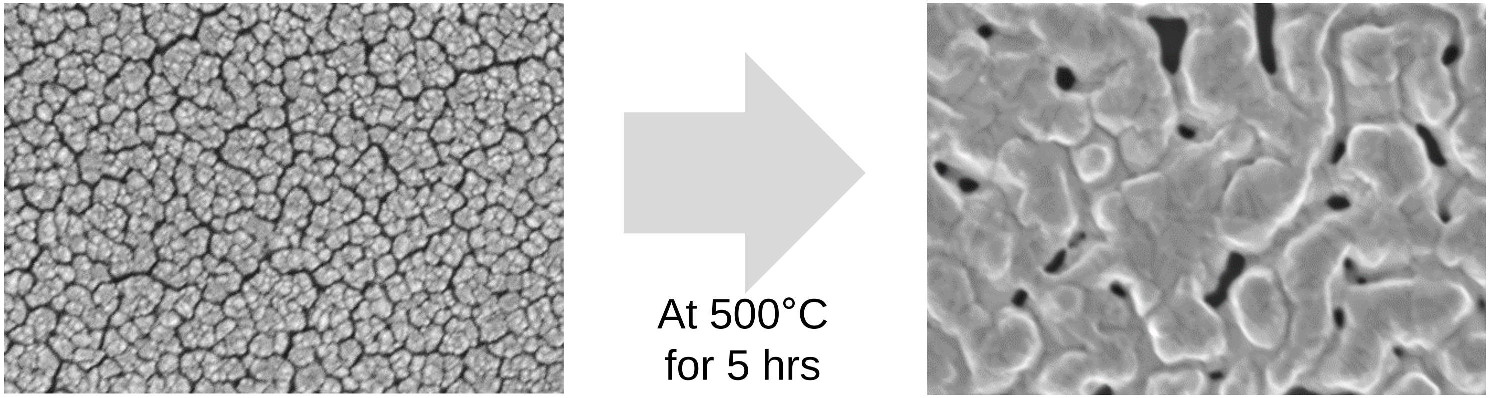
Thermal Stability over Time



Y. Jee et al. *submitted*

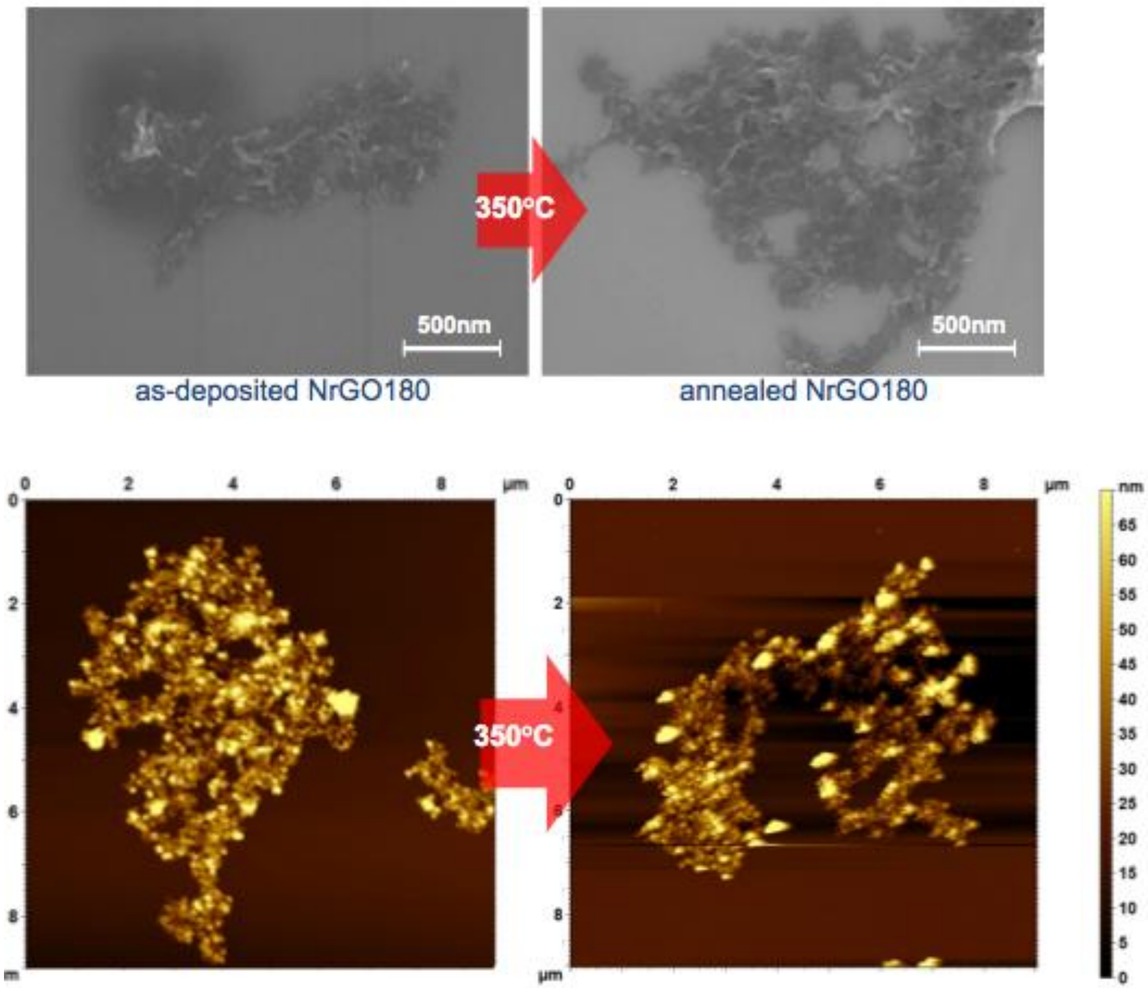
Thermal stability of Pt: accelerated agglomeration

Agglomeration of Pt



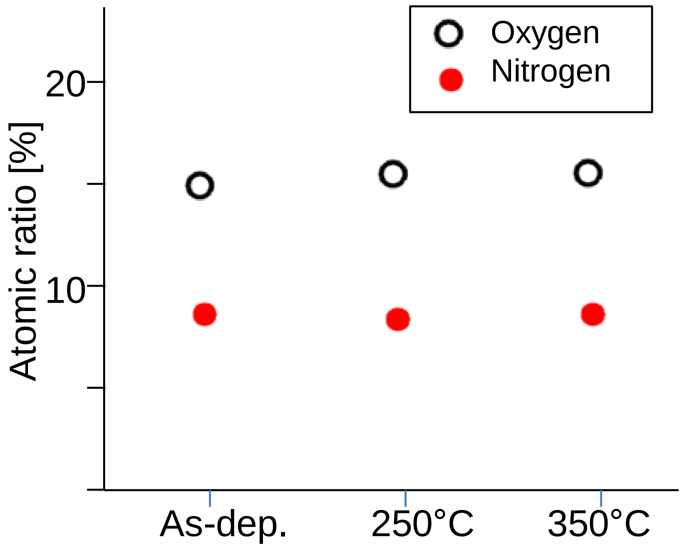
- *Ostwald ripening → Loss of active sites for ORR*

Thermal stability: morphological

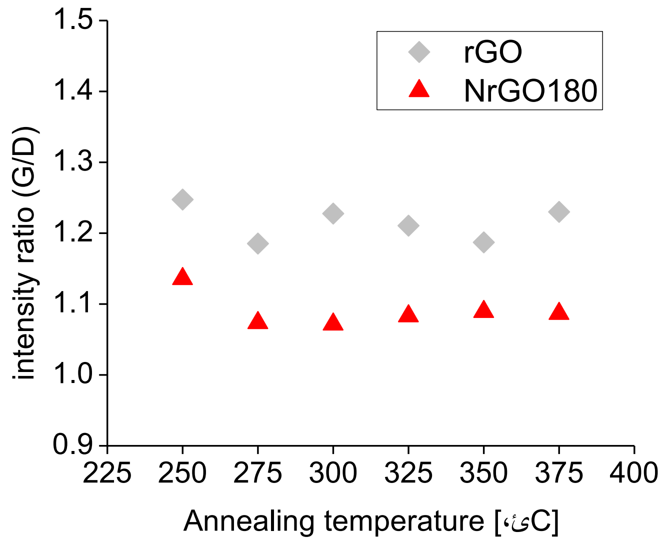


Thermal stability: defects & stoichiometry

XPS

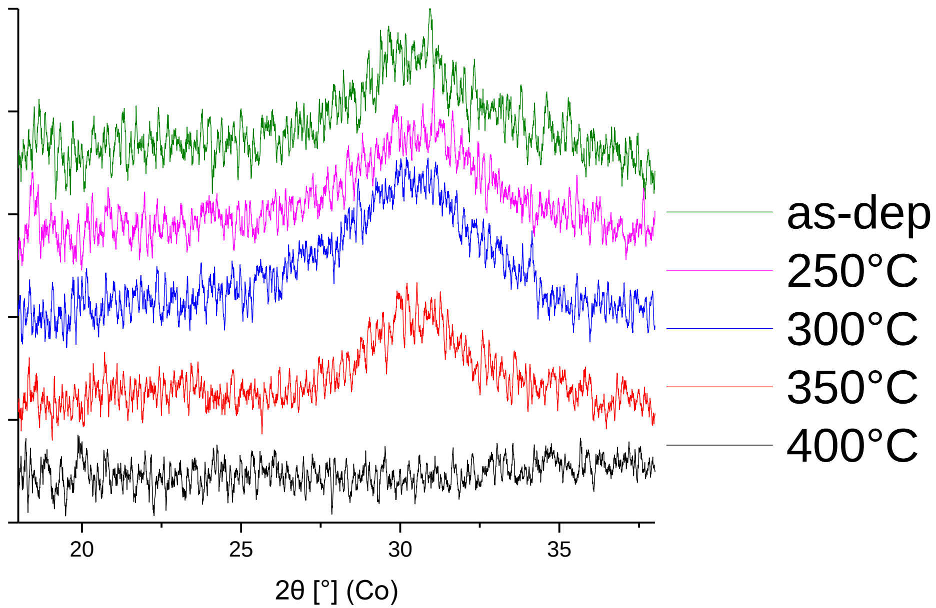


Raman



Y. Jee et al. *submitted*

Thermal stability: d-spacing



NrGO180 (As - 350°C) : ~3.4Å

Y. Jee et al. *submitted*

Transitional alternative – low loading Pt with high durability

Pt needs to have high surface area
(i.e. highly porous or nanoparticle structure)

→ Significant agglomeration during operation

→ Significant reduction in active area

→ **Needs to maintain high surface area structure**

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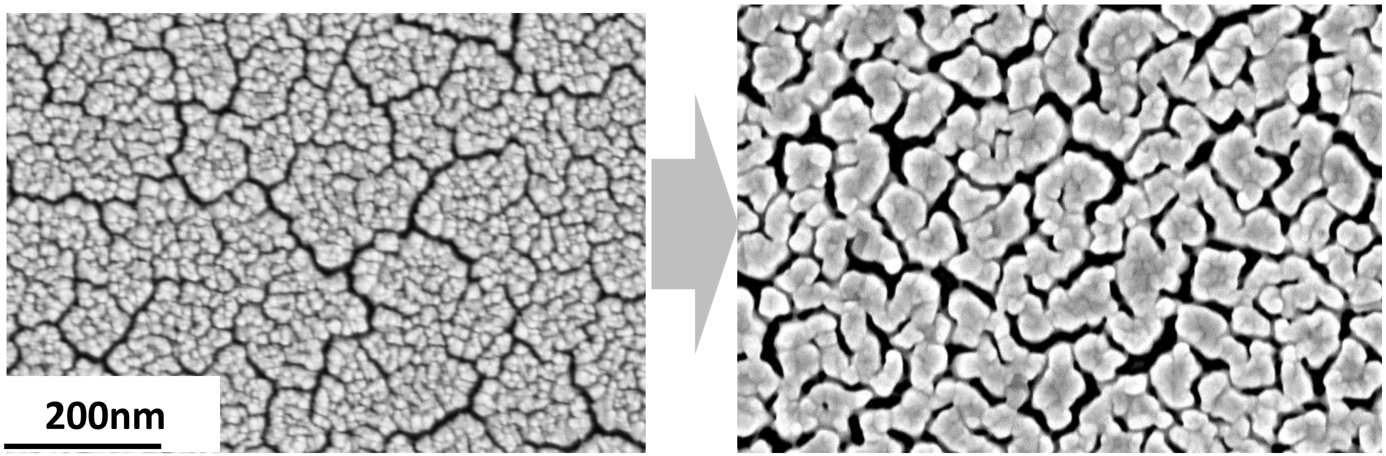
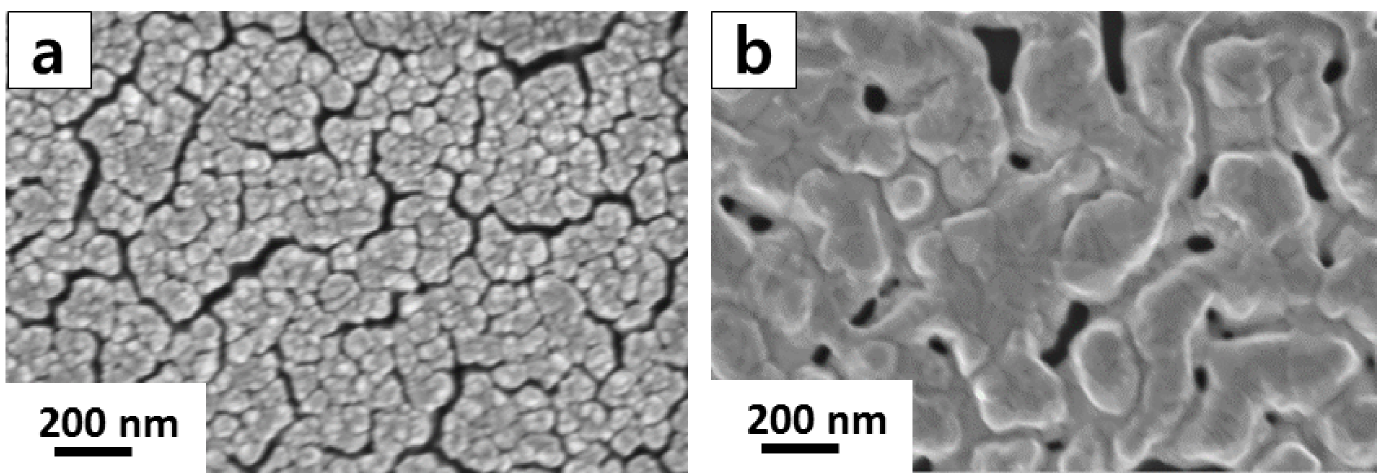
Thermal agglomeration of Pt

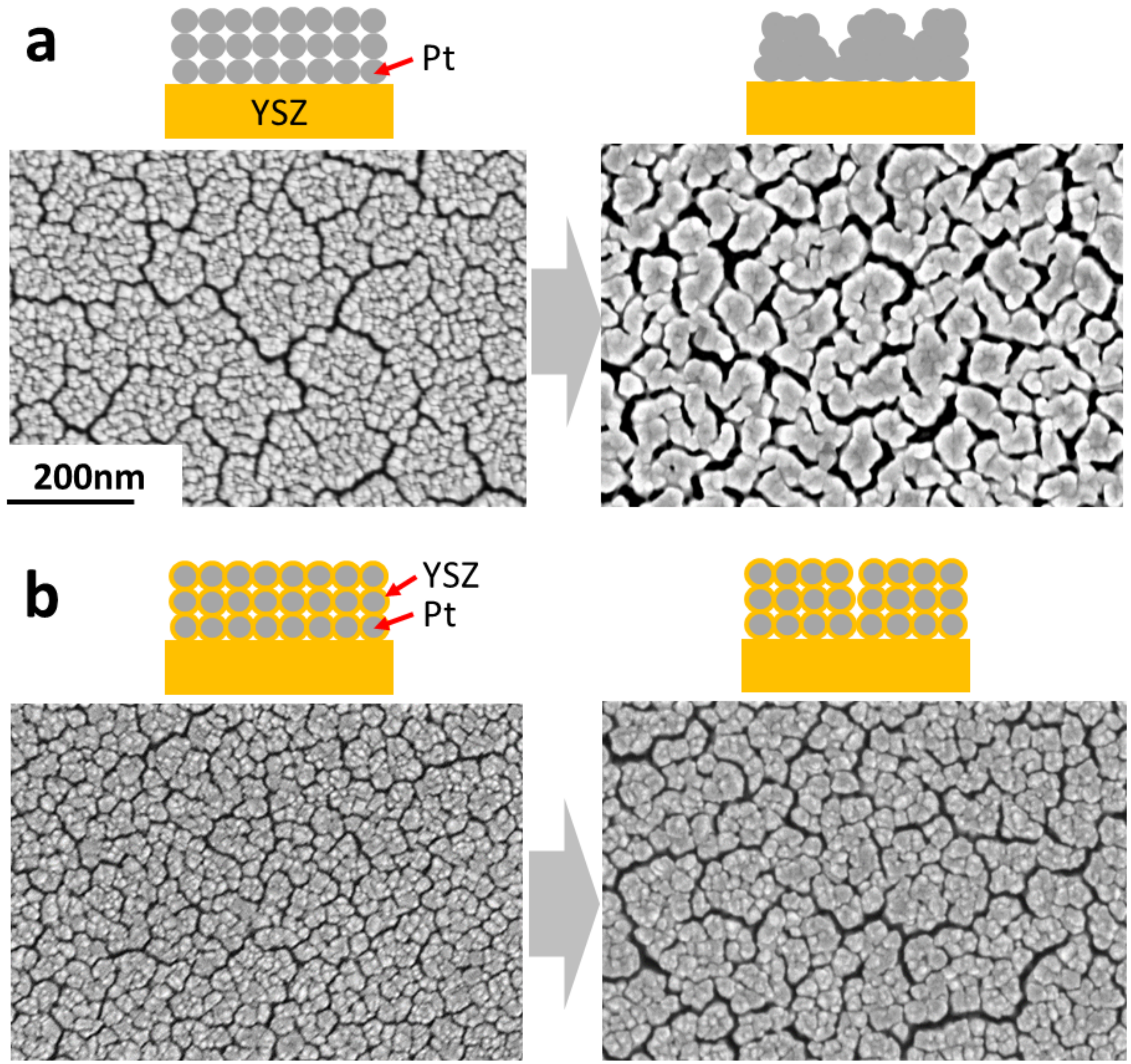
@ 500 °C



@ 600 °C



Suppression of ripening by ultra-thin oxide



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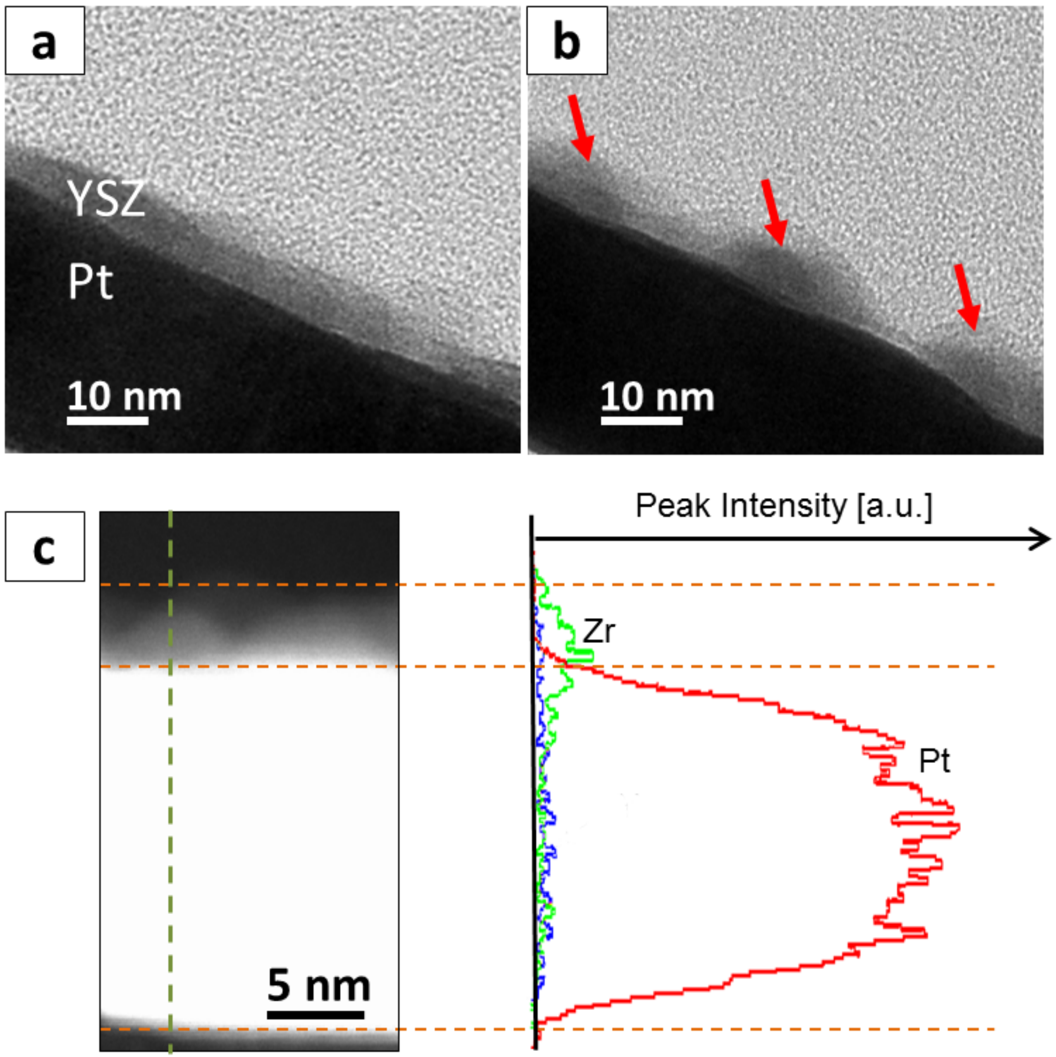

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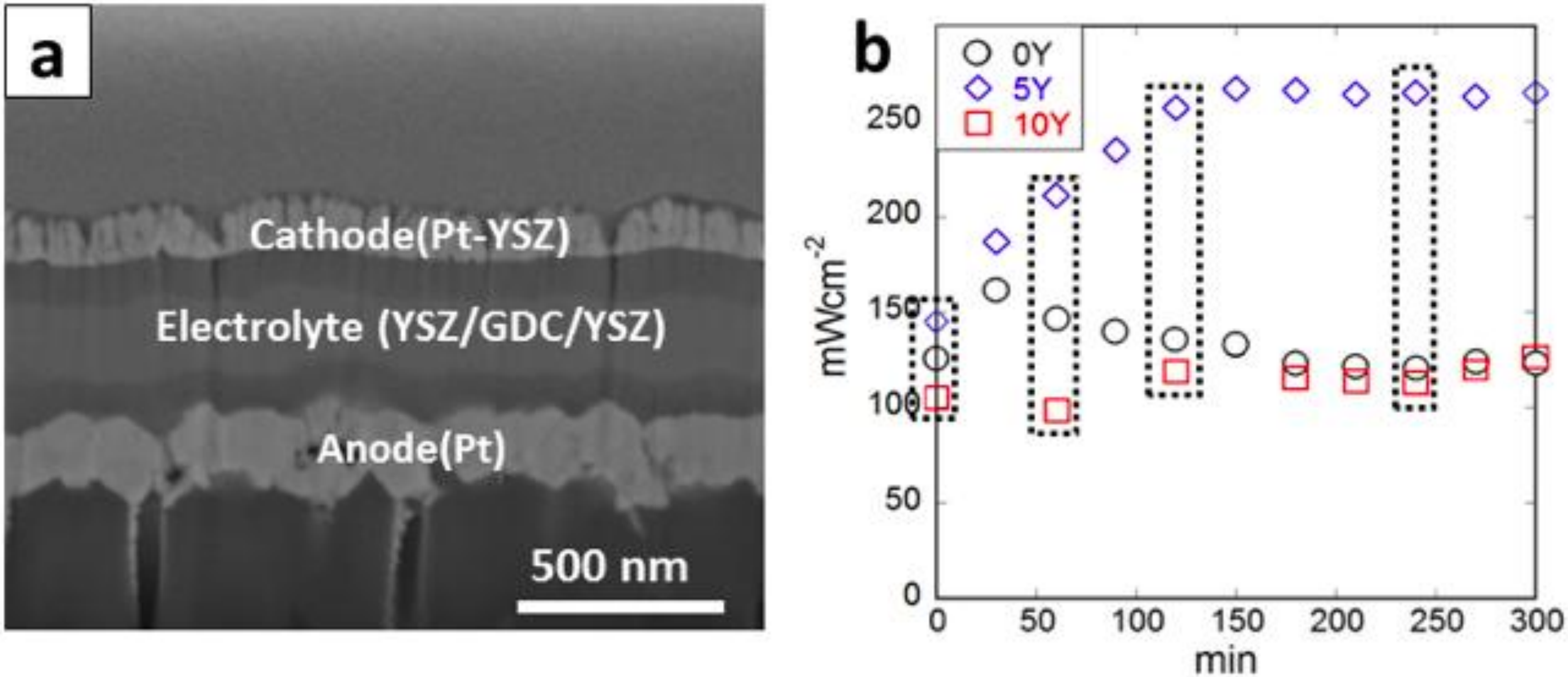
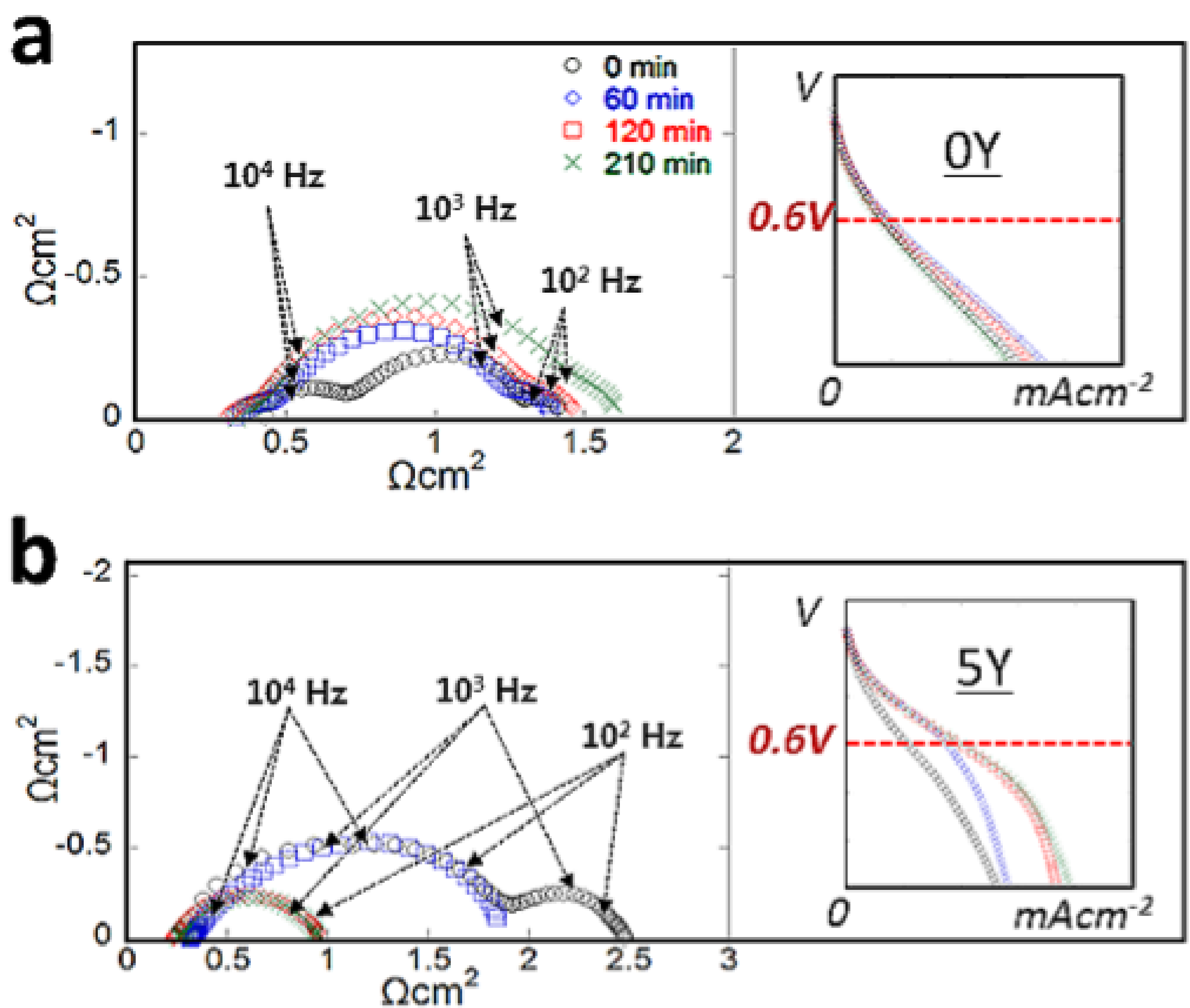


EIS analysis



Summary

- N-doped graphene as a SOFC cathod
  - showed a great oxygen reaction performance and durability at < 400 °C
  - Still much engineering opportunity (interface w/ current collector; cheaper doping process, enhanced reaction sites, etc.)

- Oxide nano-coating for metal ripening
  - Few nm oxide coating suppressed metal ripening
  - Also enhanced the catalytic activity

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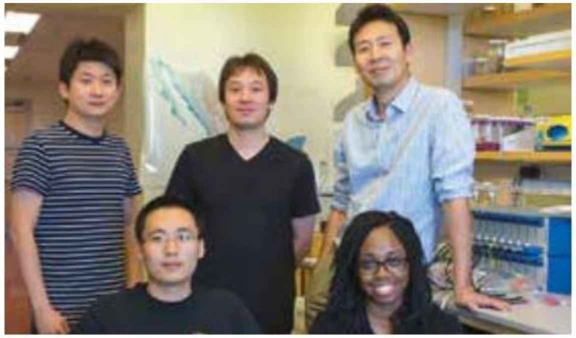


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Thank you.

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