Reduced graphene oxide as an efficient platform for rechargeable lithium batteries

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Contents

- **Introduction**

  Reduced graphene oxide (rGO) as a conducting support for rechargeable lithium batteries

- **Recent result of our group**

  I. **rGO as a electrical conducting platform for high power lithium ion battery**

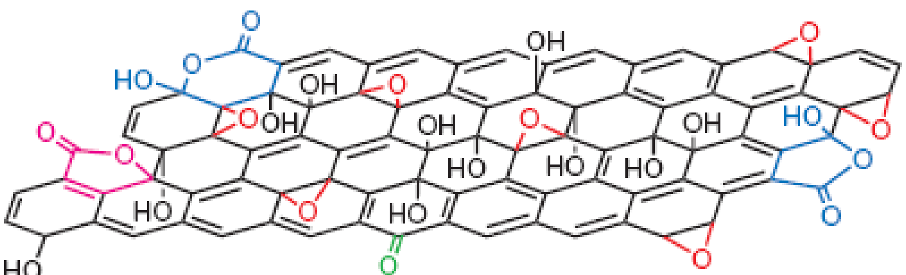
  II. **rGO as an efficient catalyst support for Li-air cells : Study on the catalytic activity of noble metal-RGO hybrids in Li-air cel**

- **Summary**

rGO as a conducting support for lithium batteries

❖ **Reduced graphene oxide (rGO)**

— **A derivative of graphene. Reduced from graphene oxide**



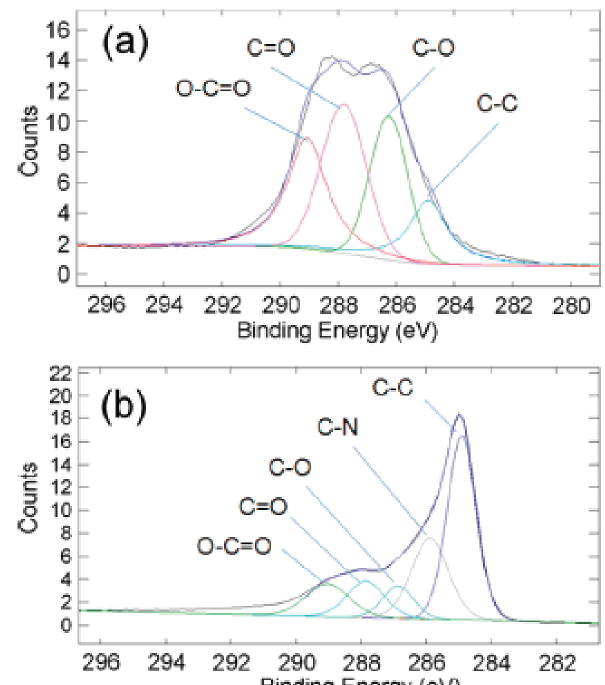
Graphene oxide : oxidized graphene

Reduction to restore graphitic structures (chemically or thermally)

— **The reduction cannot completely recover graphitic structure in graphene.**

— **Thus rGO is a defective graphene with some oxygen functionalities.**

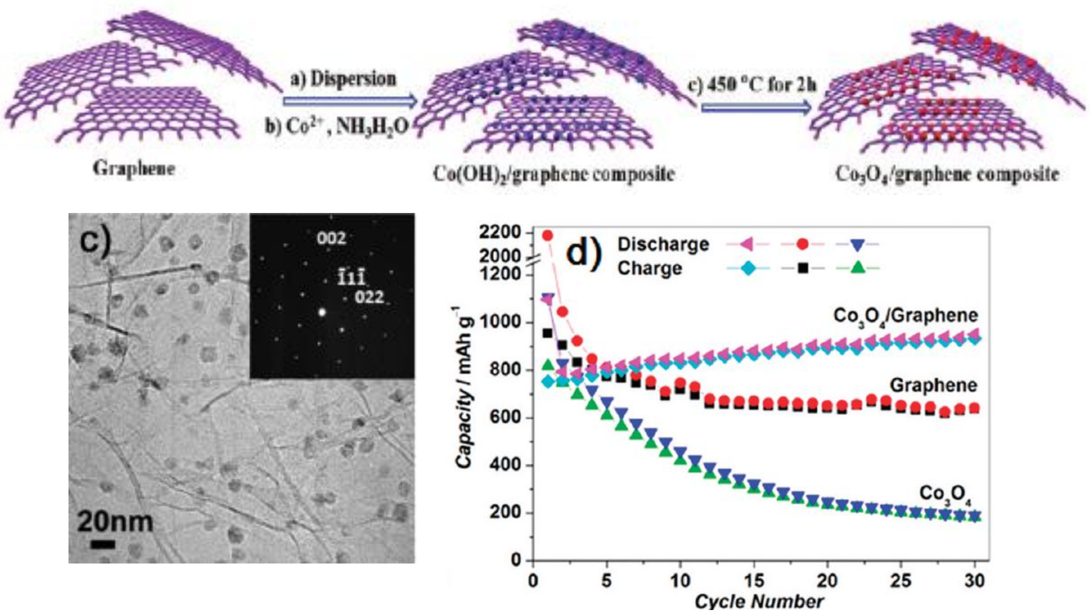
— **Though not conductive as perfect graphene, rGO is conducting.**



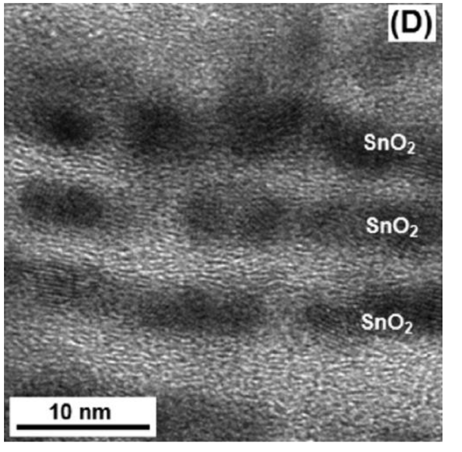
ACS Nano (2010), 4(7), 3845-3852

rGO as a conducting support for lithium batteries

❖ **Oxygen functional groups can be utilized as anchoring sites for particle growth leading nanoparticle growth in 2-D conducting rGO**



ACS Nano (2010), 4(6),3187-3194

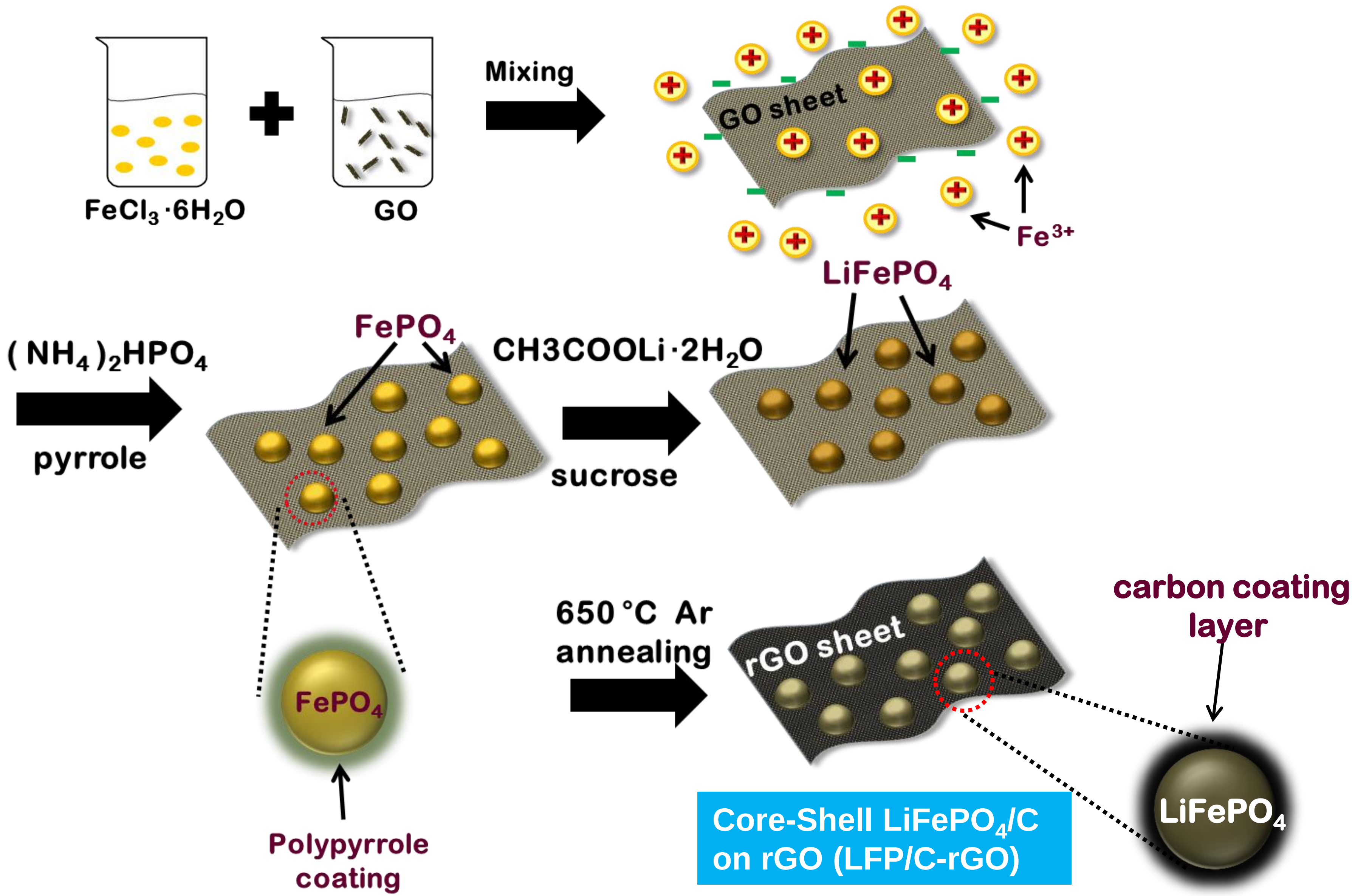


ACS Nano (2010), 4(3),1587-1595

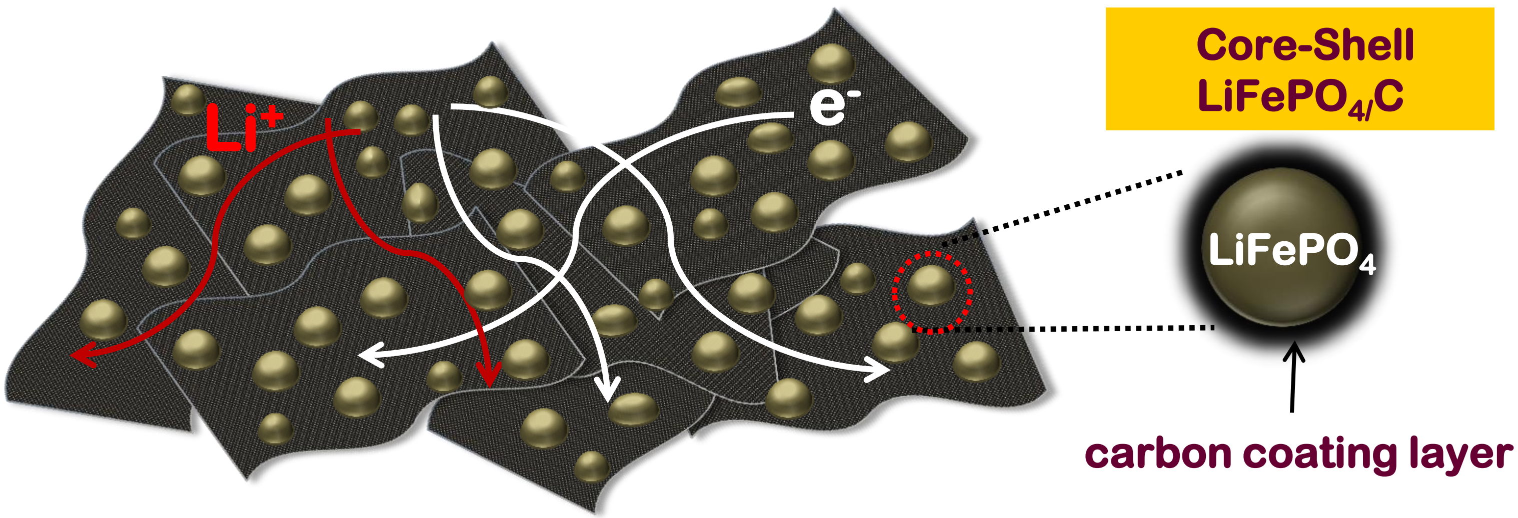
Co_3O_4-rGO, SnO_2-rGO, MnO_2-rGO hybrid anode showed superior rate capability and cycling stability due to nanosizing and facile electron transport through 2 D sheets

I. rGO as an electrical conducting platform for high power lithium ion battery

Synthesis of Core-Shell $LiFePO_4$/C-rGO (LFP/C-rGO)



Role of rGO

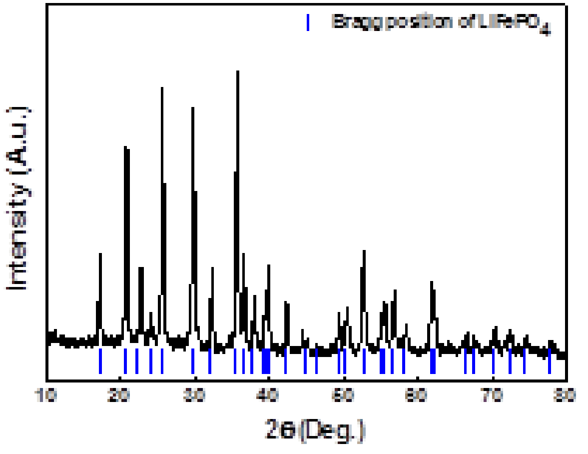


- RGO provides efficient **electrical pathway** for electrons
- Active material growth on rGO sheets inherently restrict particle growth : platform for nanoparticle growth

Enable High Power Capability!

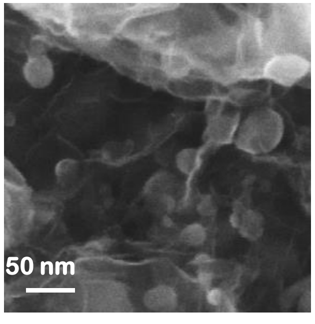
Structural Analysis of Core-Shell $LiFePO_4$/C-rGO

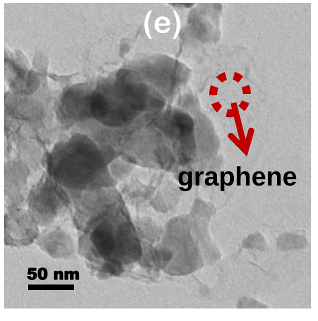
XRD

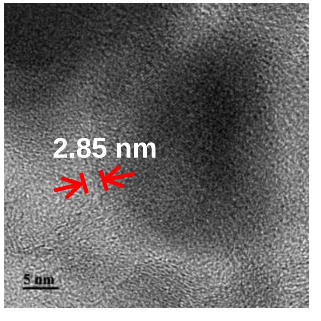


- Highly crystalline $LiFePO_4$

SEM, TEM



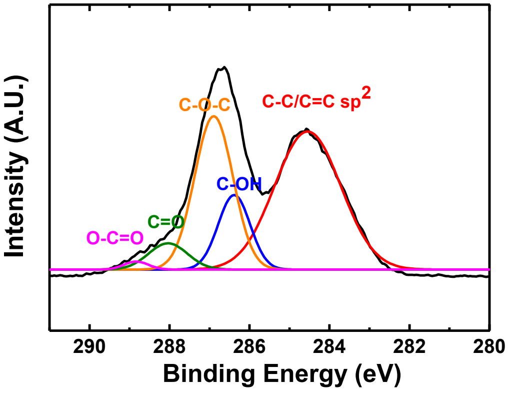




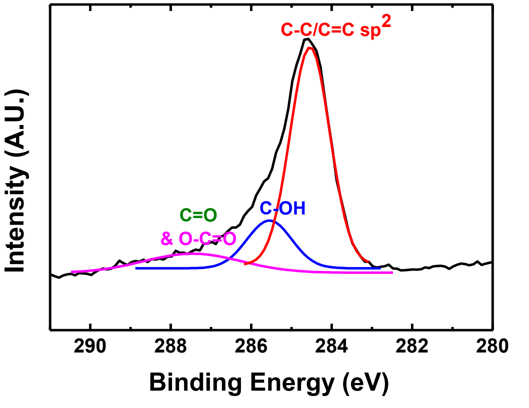
- Core-shell carbon coated (~ 3 nm) $LiFePO_4$ nanoparticles (30~40 nm) loaded on rGO

XPS

before anneal: GO



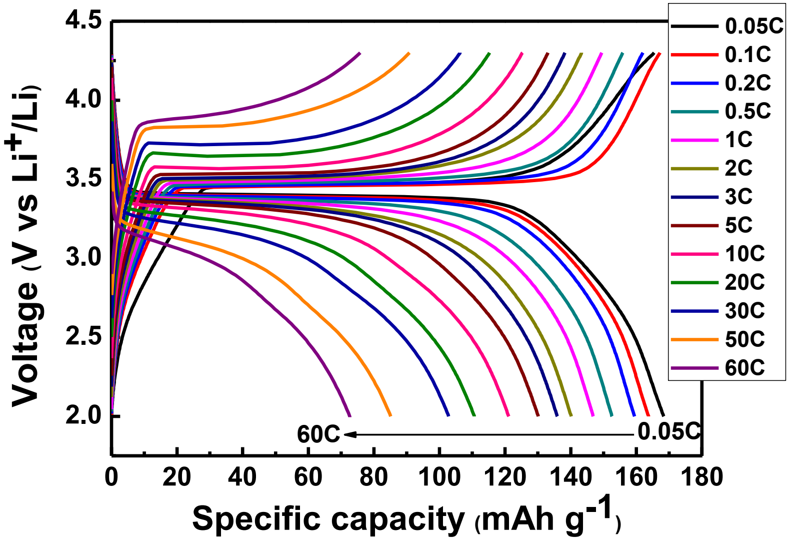
after anneal: rGO



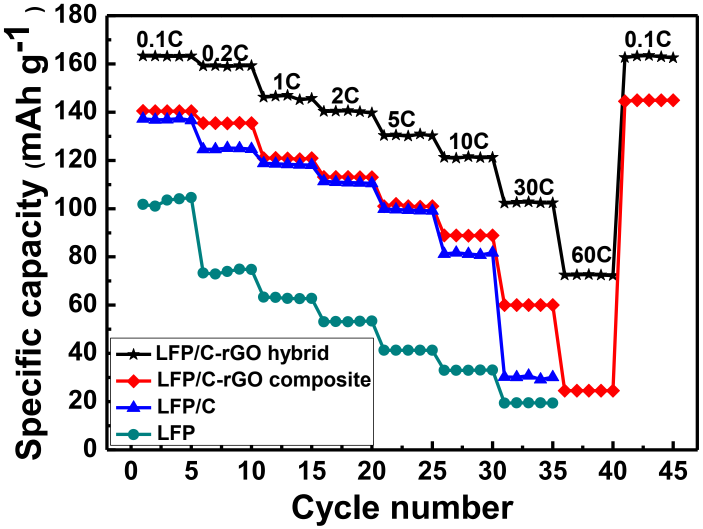
- GO successfully reduced to rGO

High Power Performance of LFP/C-rGO

Charge-discharge curves of LFP/C-rGO



Comparison of rate capability

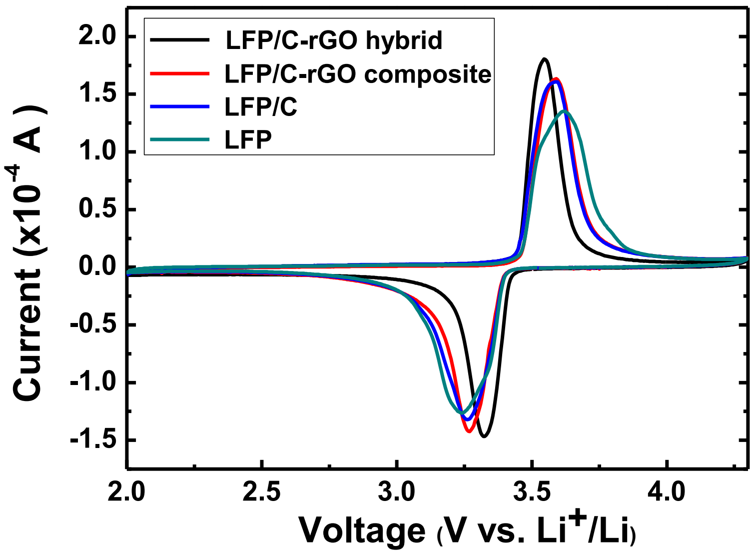


- **LFP/C-rGO showed much higher capacity at high rates : Superior high power performance (rate capability)**

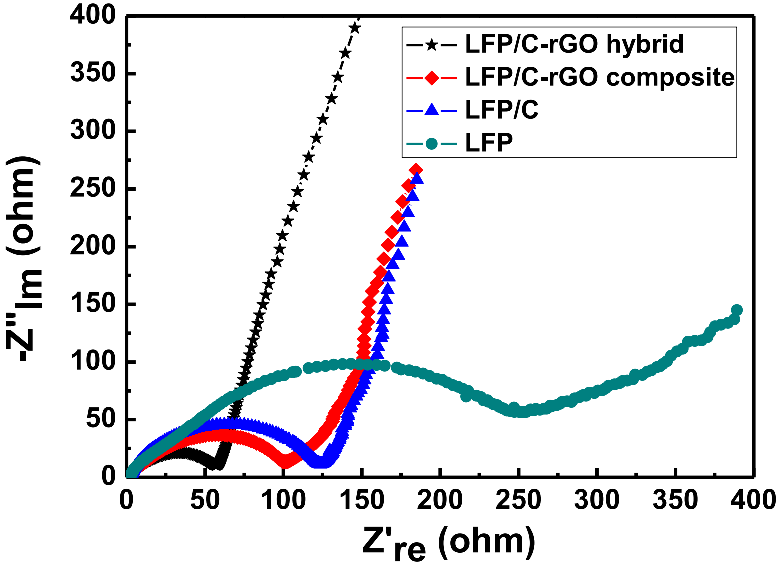
Superior high power performance due to true nanoscale LFP/C active material-rGO conducting support composite formation

High Power Performance

Cyclic Voltammetry



Impedance



LFP/C-rGO hybrid

- Potential interval is the smallest
- Current highest

LFP/C-rGO hybrid

- Smallest semicircle =lowest Ohmic resistance

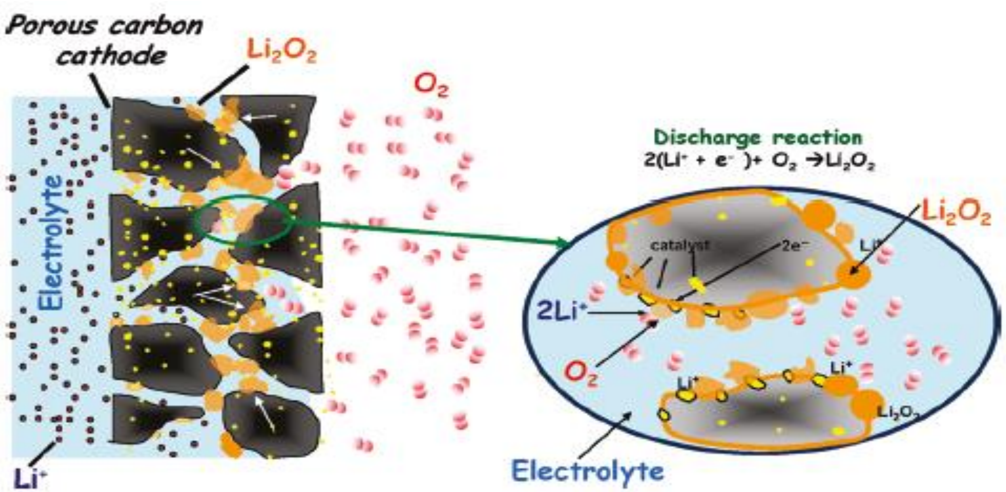
Better kinetics and lower resistance resulting from fast electron supply

II. rGO as an efficient catalyst support for Li-air cells

Rechargeable Li-Air Batteries

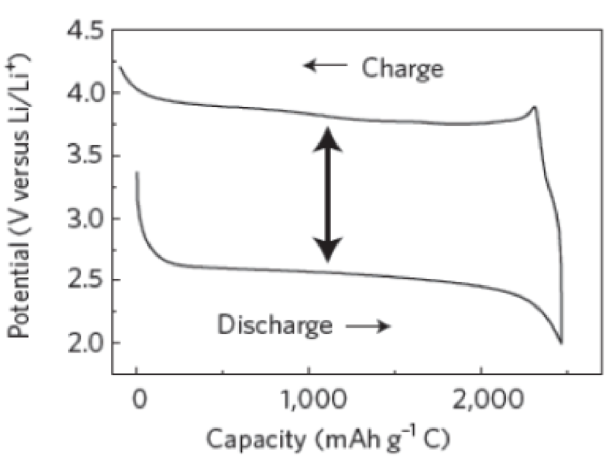
- Fundamental cathode reaction in aprotic Li-Air Batteries

  $2Li + O_2 \leftrightarrow Li_2O_2$



J. Phys. Chem. Lett. (2011), 1, 2193-2203

- High theoretical capacity:
  - 11,420 Wh kg^{-1} (oxygen only)
  - 3500 mAh g^{-1} (Li_2O_2 only)

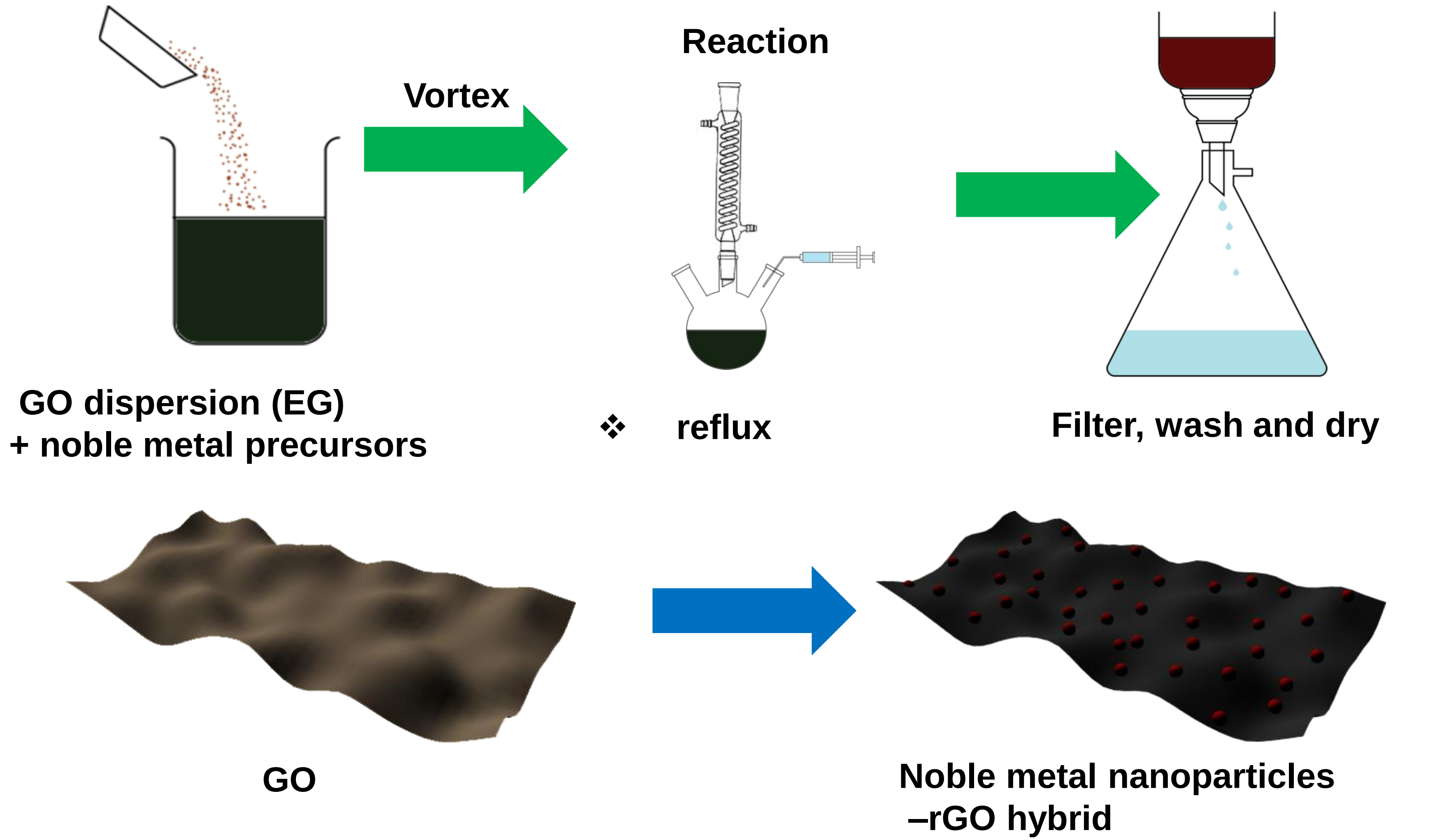


- Cathode… ge o… …ntial,
  lea…
  - ✓ Co…
  - ✓ D… …g necessary

Catalyst loaded on rGO support

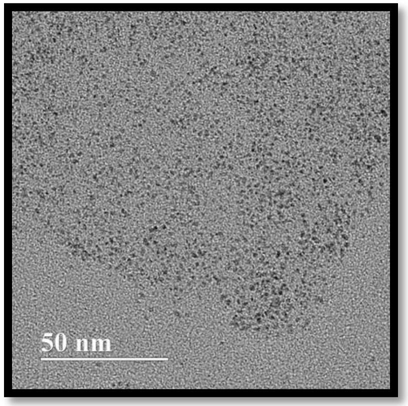
Noble Metal Nanoparticles Supported on rGO

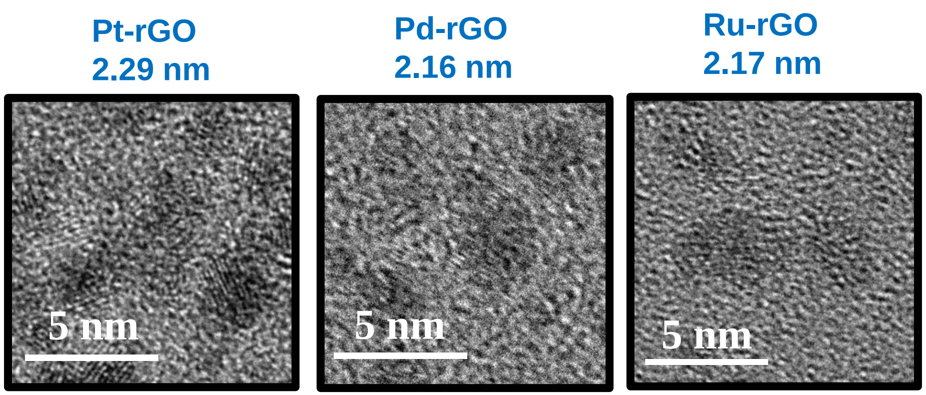
❖ **Pt, Pd, Ru-rGO: polyol synthesis**



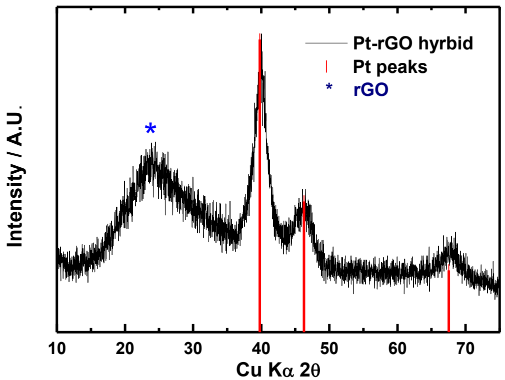
Structural Analysis(1)

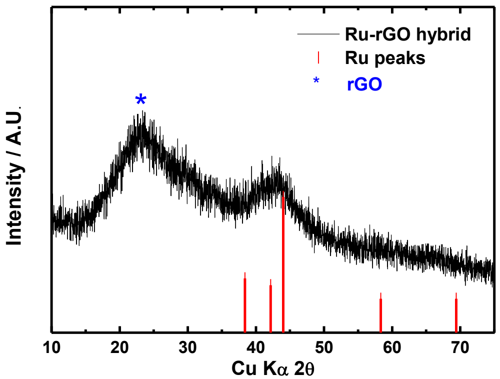
❖ Average particles size: ~2.2 nm





❖ Nanocrystalline metallic + rGO by XRD





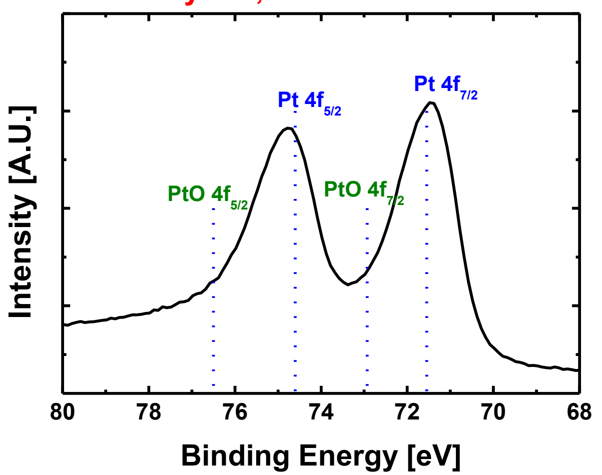
❖ Mass content: ~ 50 wt %

(Pt 49 wt%, Pd 45 wt%, Ru 46 wt%)

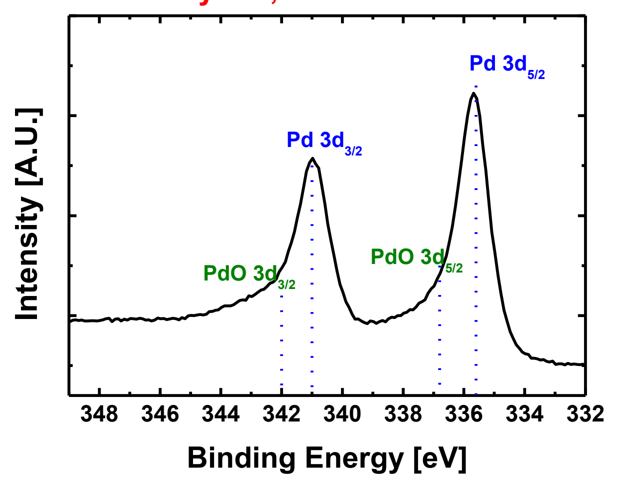
Structural Analysis(2)

❖ Surface oxidation by XPS

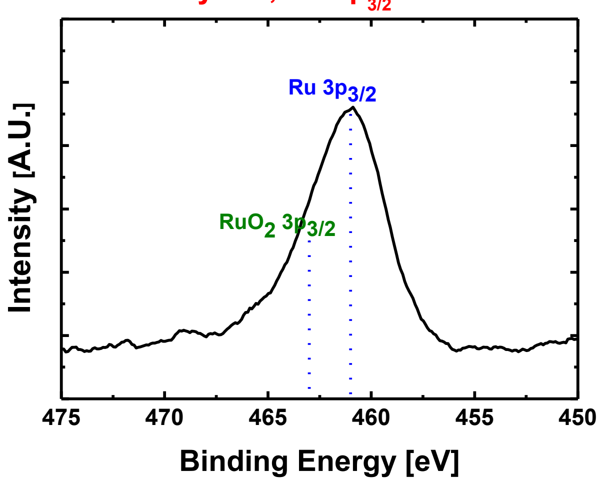
Pt-rGO hybrid, Pt4f



Pd-rGO hybrid, Pd3d



Ru-rGO hybrid, Ru $3p_{3/2}$

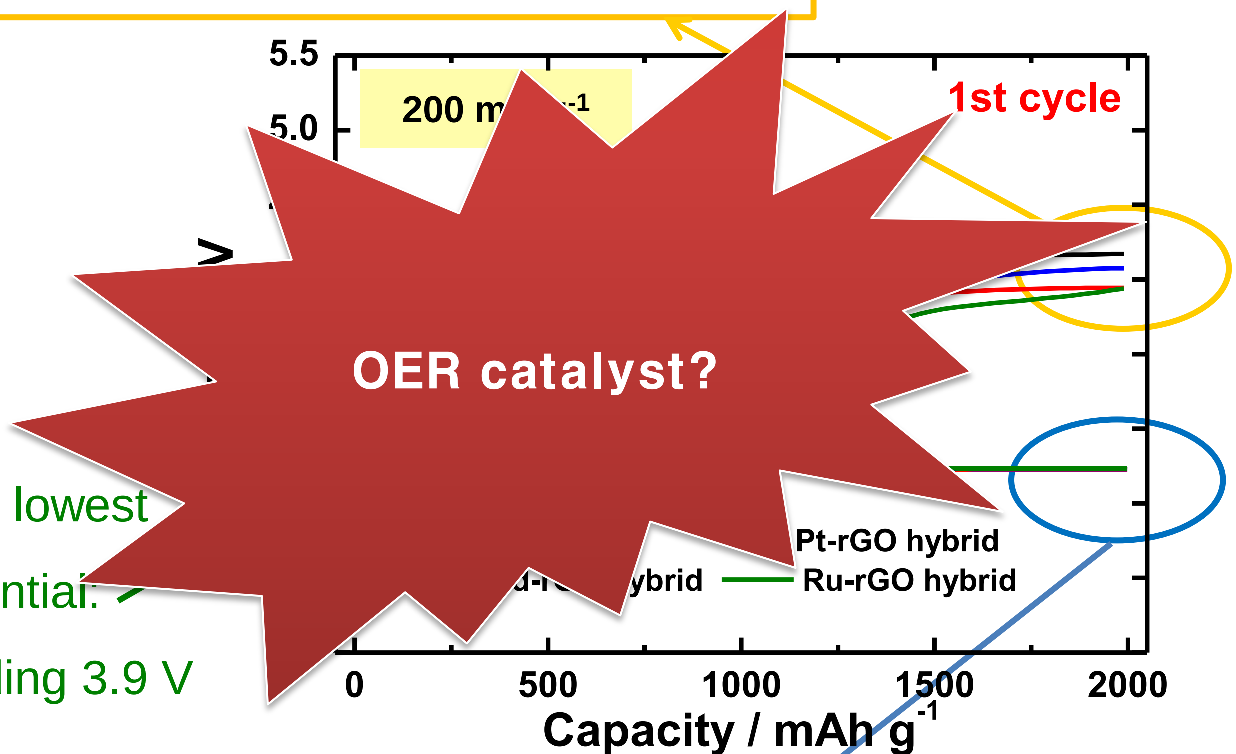


Main peaks corresponds to metallic noble metals
: No significant surface oxidation

Catalytic Activity in Li-Air Batteries

OER charge

- All noble metals: showed lower overpotentials

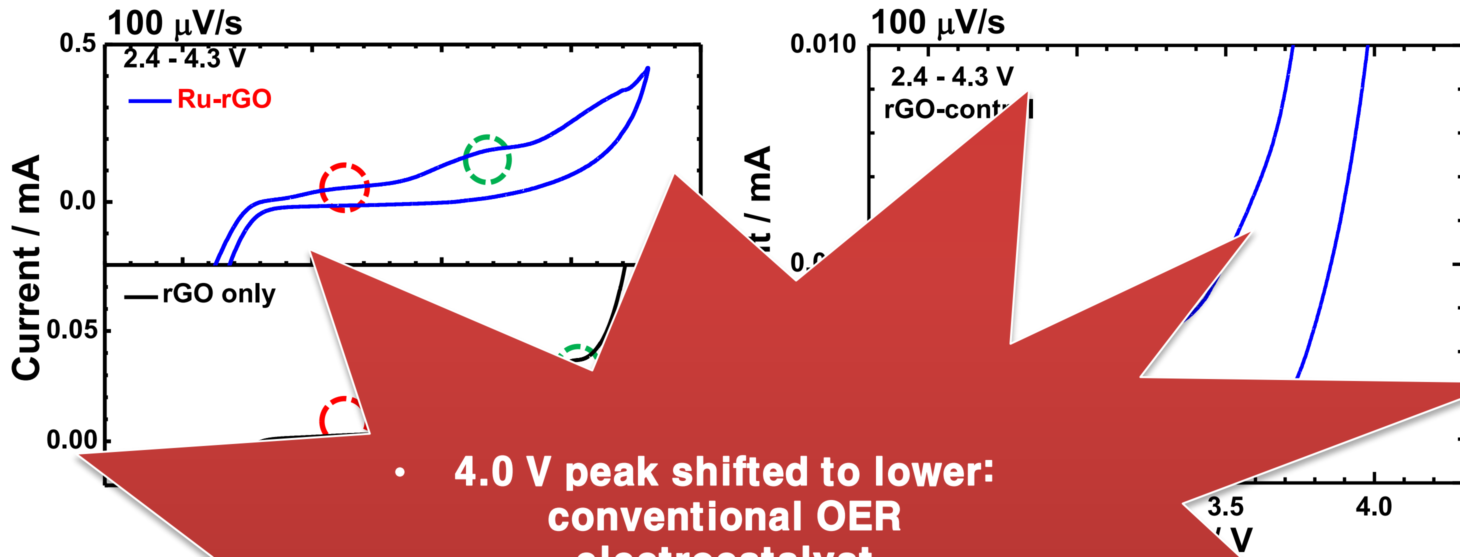


Ru-rGO showed lowest charge overpotential: Avg. ~3.5 V, ending 3.9 V

ORR discharge

- Did not change much with the presence of noble metals

Catalytic Mechanism of Ru-rGO



- 4.0 V peak shifted to lower: conventional OER electrocatalyst
- 3.2 V peak invariant: Not conventional electrocatalyst ?

Point

1. Higher cu… …dic scan… …hanced reactions in both for… …discharge products.

2. For oxidation pe…

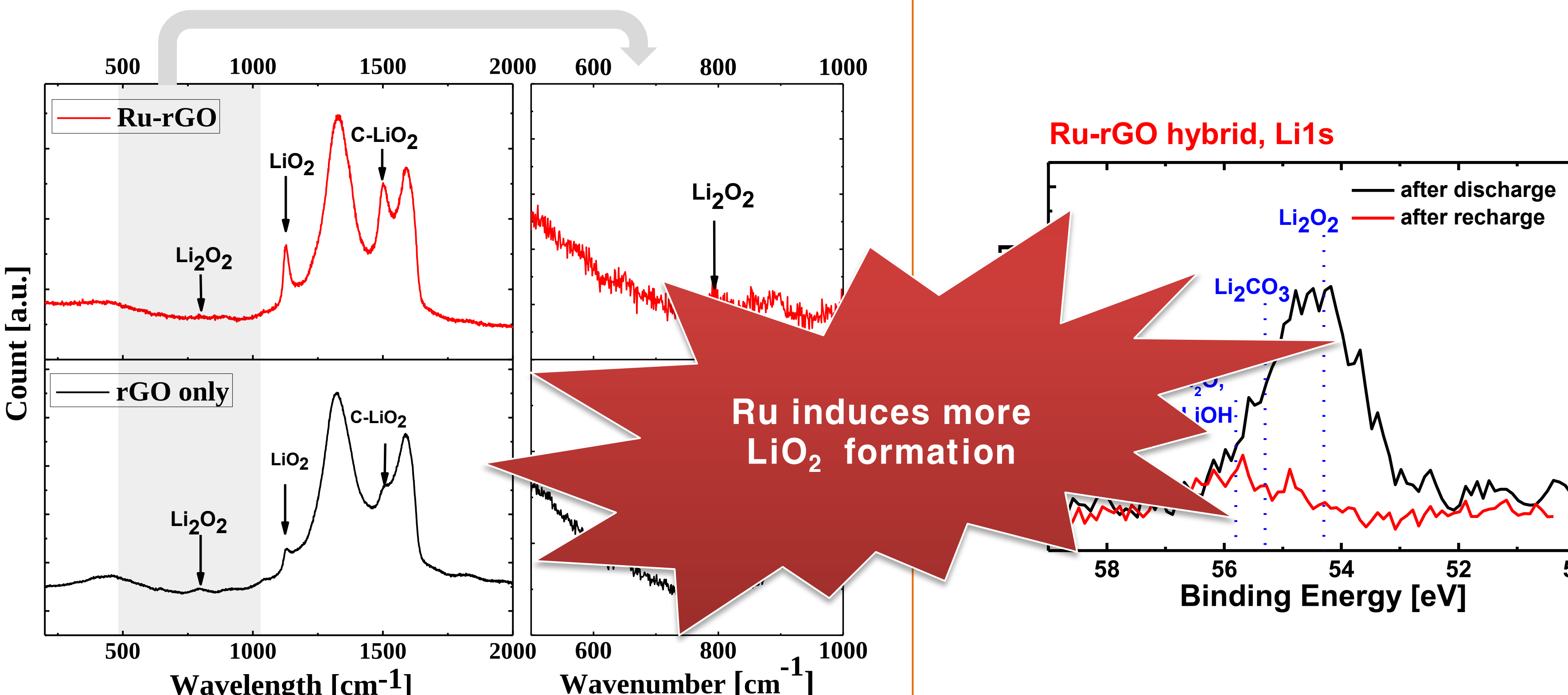
   ① Onset potential at 3.2 V: identical to rGO

   ② Peak of rGO at 4V was shifted to 3.7 V

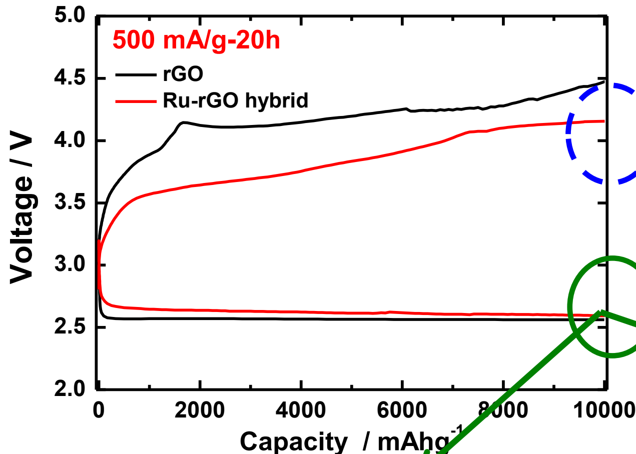
Identification of Discharge Products(1)

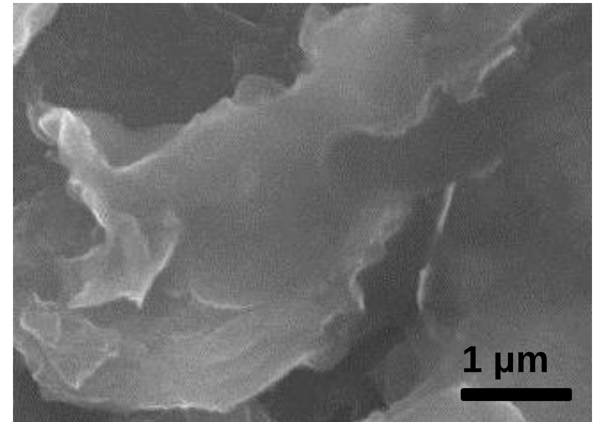
- **No crystalline peak from powder XRD: amorphous**
- **Discharge products analyzed by Raman and XPS**

Raman | XPS



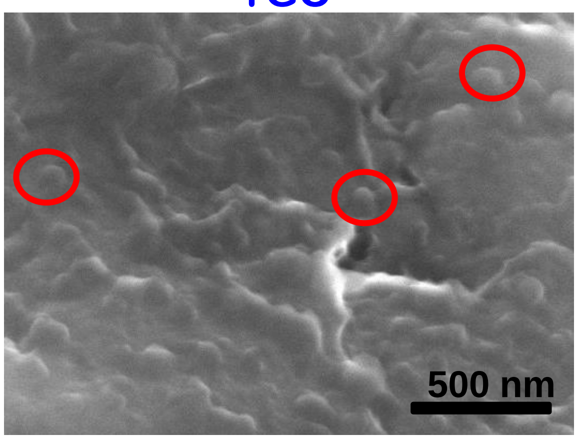
Morphology Trace





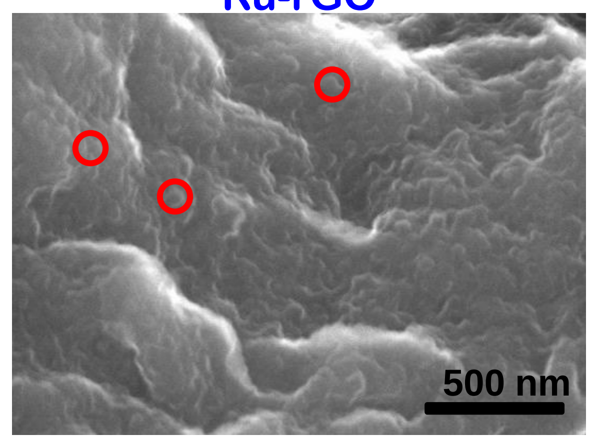
Upon charging: completely decomposed

rGO



Discharge products: ~100 nm

Ru-rGO



Discharge products: <~50 nm

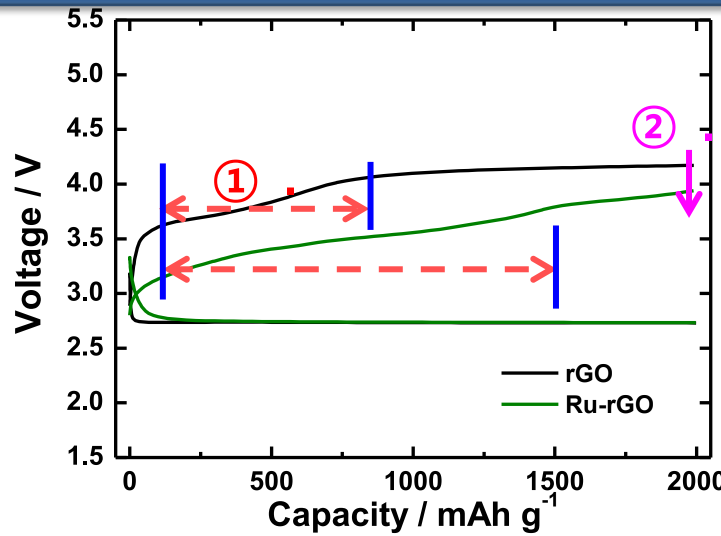
*Since the current density test is already quite high (400 µA cm^{-2}), discharge particles are not toroids, but feature size is clearly smaller for Ru-rGO!

Nano Letters, accepted (2015)

Suggested Mechanism of Ru-catalysts

The discharge products are mixture of stoichiometric Li_2O_2 and defective or smaller sized Li_2O_2/or the superoxide LiO_2. The amount of LiO_2 largely depends on the kinetic parameters during discharge.

Catalysts might have stronger binding with oxygen or superoxide providing more nucleation sites & leading LiO_2 or poorly crystalline, small-sized Li_2O_2 structure.



- Dual role of catalyst

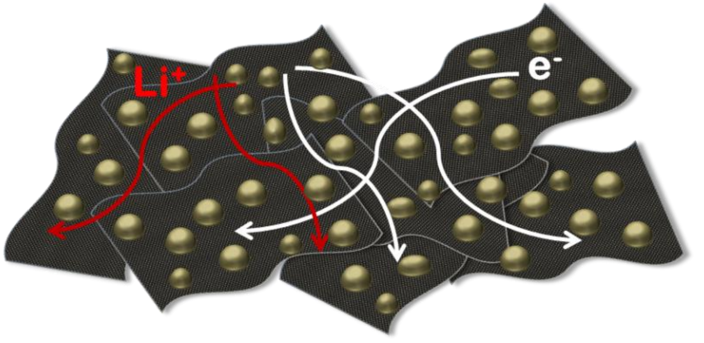
① During ORR
- Control the nature of the discharge products
- Favor the formation of defective, smaller sized Li_2O_2

Extend the lower potential region

② During OER
- facilitate the decomposition of stoichiometric Li_2O_2 that might be present in the discharge product

Summary

- rGO served as a efficient electrical pathways to enable high power performances in LIB



- rGO enabled very uniform, nanosized noble metal catalyst (~2 nm) synthesis on its surface. Resulting catalyst system reduces charge overpotentials in Li-air cells