Design of Carbon-based Oxygen Reduction Electrode for Fuel Cell

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Contents

Thermodynamics in PEMFCs

Anode : $H_2 \rightarrow 2H^+ + 2e^-$ (0 V) Hydrogen oxidation reaction (HOR)
Cathode : $1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O$ (1.23 V) Oxygen reduction reaction (ORR)

Total : $H_2 + 1/2O_2 \rightarrow H_2O$ (1.23 V)

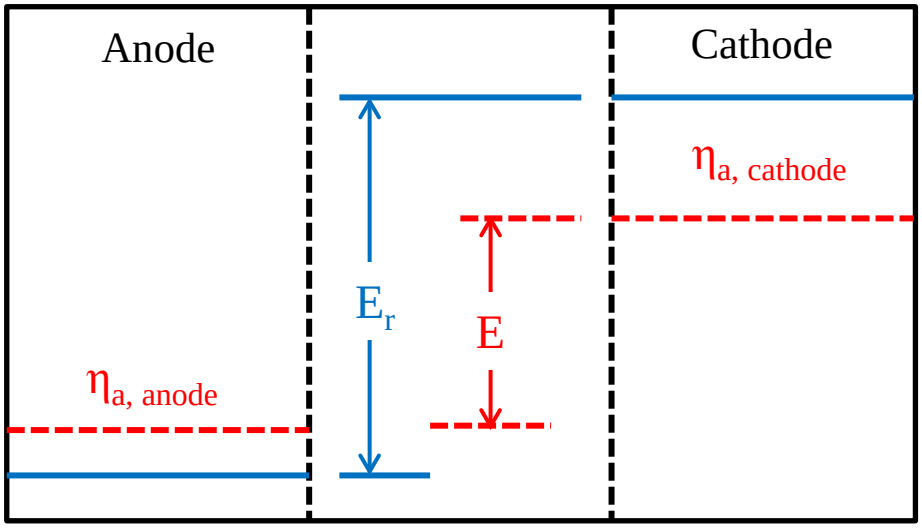
Reversible cell potential = 1.23 V

Activation loss in PEMFCs

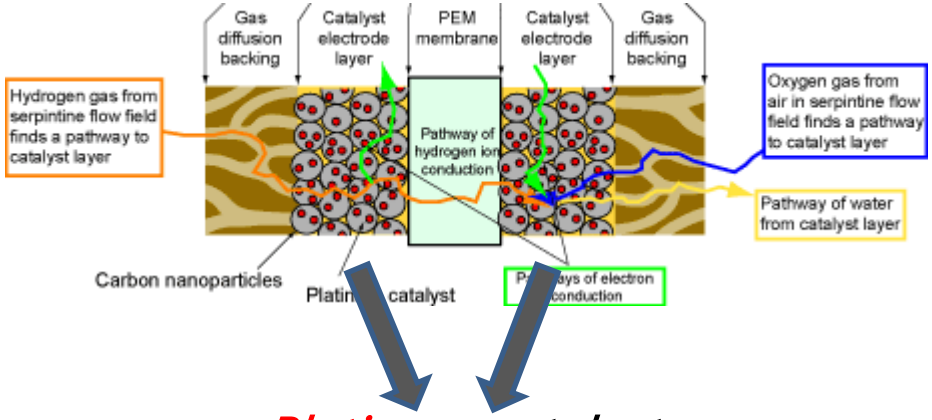
Anode (HOR): $H_2 \rightarrow 2H^+ + 2e^-$
Cathode (ORR): $1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O$

HOR << ORR

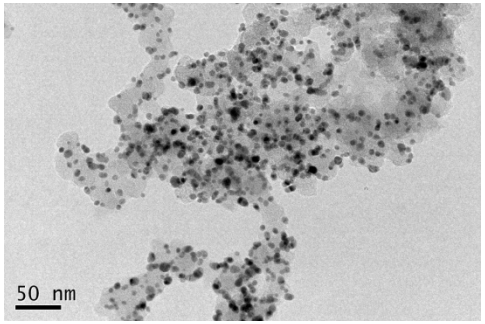
It needs catalysts!



Problems



Platinum catalysts



$ 1,200,000

Various Alternatives

1. Lean-Pt catalysts
   e.g. Pt-M alloys
2. Noble metal catalysts
   e.g. Pd, Ir, or Ru
3. Transition metal catalysts
   e.g. TiN, CoSe, WC
4. Non-metal catalysts
   e.g. Carbon based catalysts

[Purpose of the research]

1. Find carbon based catalyst having ***high ORR activity*** with ***cheap price***.

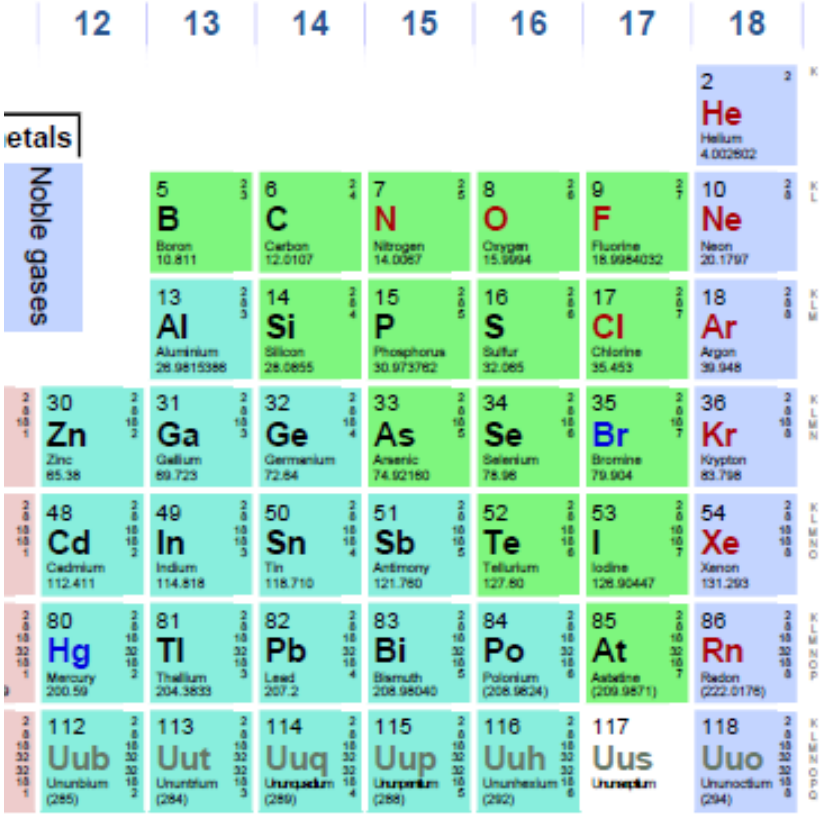
Binary and Ternary Doping of Nitrogen, Boron, and Phosphorus into Carbon for Enhancing Electrochemical Oxygen Reduction Activity

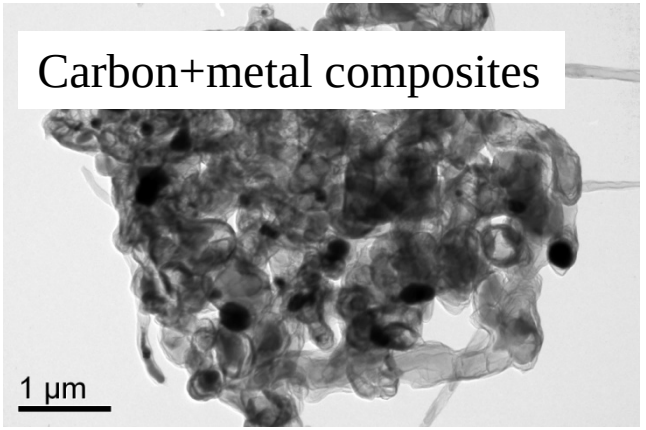
ACS Nano 6 (2012) 7084-7091

Purpose of the study

A new strategy for enhancing ORR activity

Additional doping of heteroatoms





Acid treatment
with aqua regia

Final catalysts

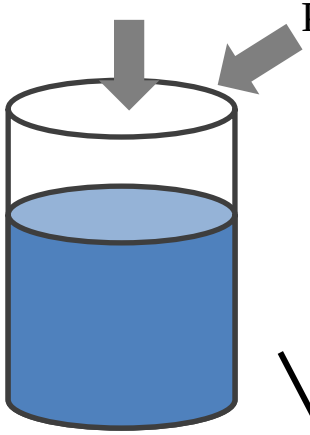
1. NDC: N-doped carbon
2. Dual doped carbon
    1. B,N-doped carbon
    2. P,N-doped carbon
3. Ternary doped carbon
    1. B,P,N-doped carbon

***Preparation** of catalysts*

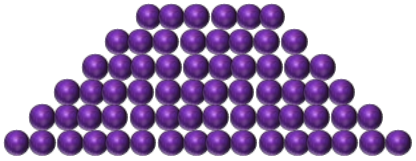
1. Homogeneous powder

Dicyandiamide
$FeCl_2$ & $CoCl_2$

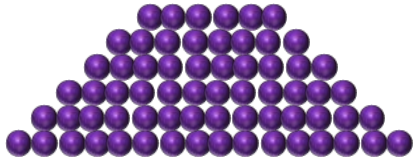
Boric acid or
Phosphoric acid



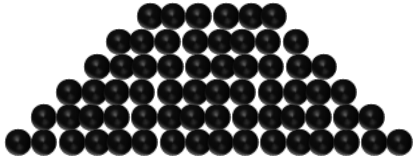
Evaporation of water



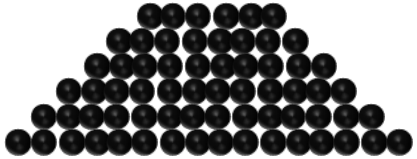
2. Carbonization



Pyrolysis, 900 °C



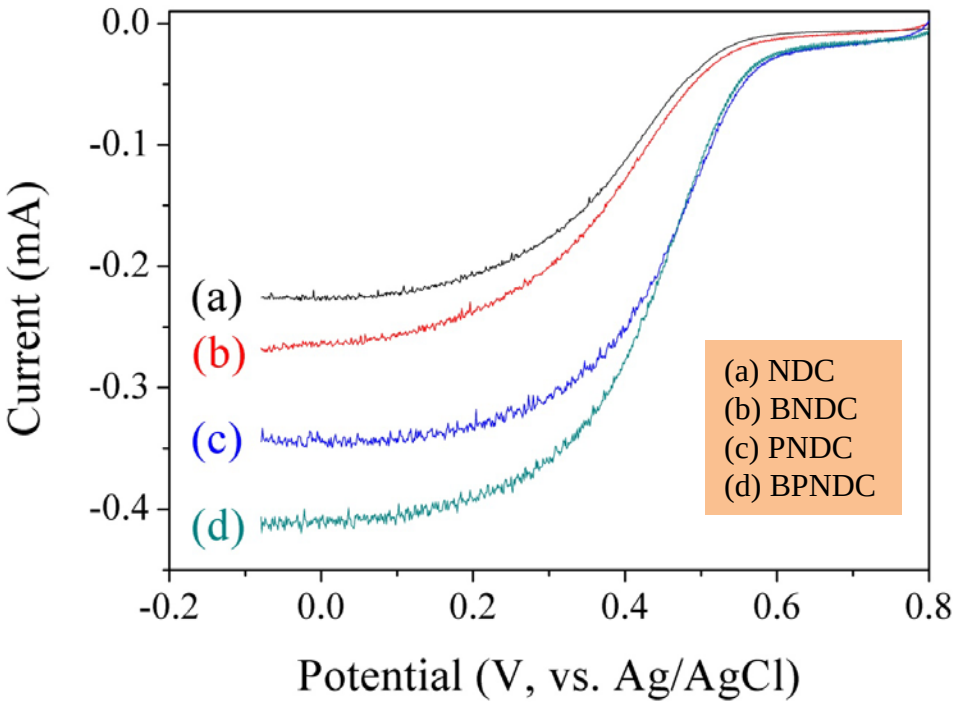
Acid treatment

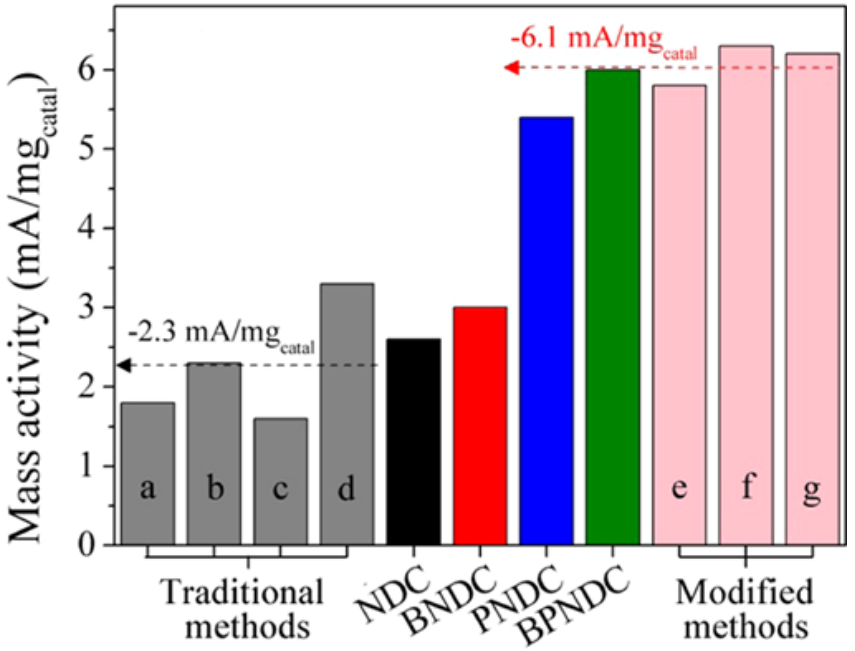


**** Abbreviations***

NDC, BNDC, PNDC, and BPNDC

ORR activities of the prepared catalysts



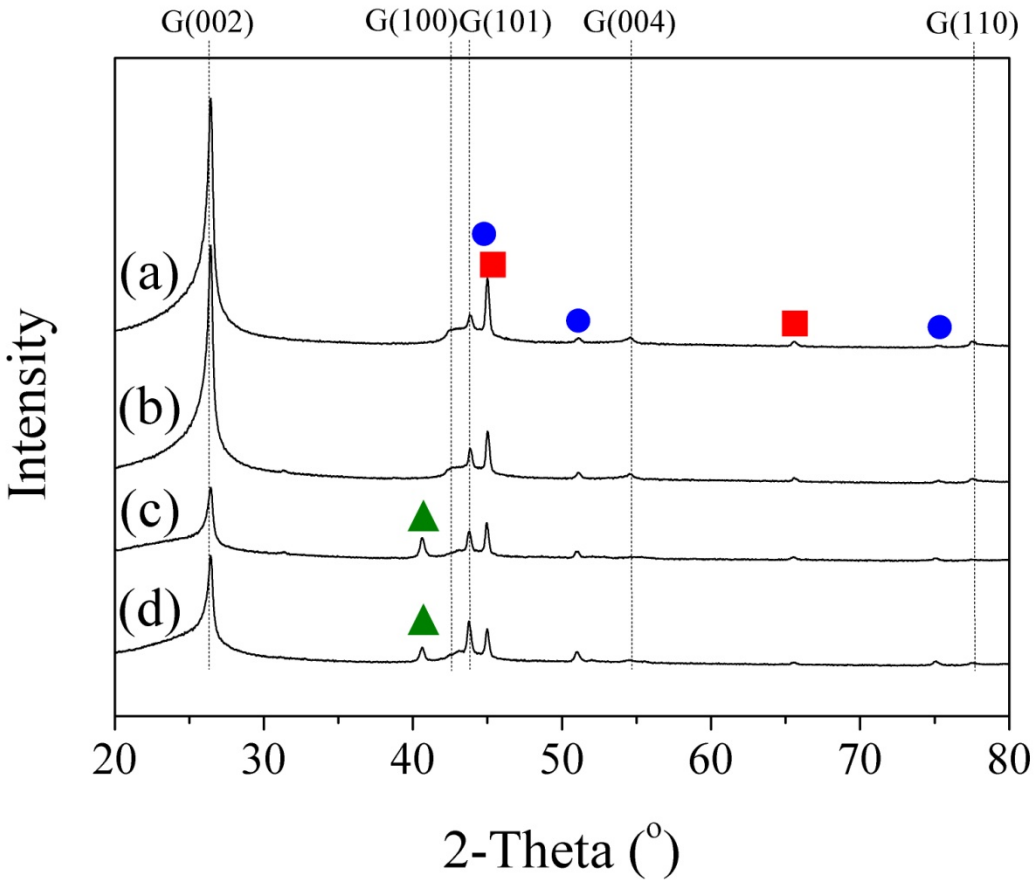


1. Conditions : 2000 rpm, 1M $HClO_4$, 5 mV/s
2. Onset Potential : 0.6 V (vs. Ag/AgCl)
3. ORR activity : BPNDC > PNDC > BNDC > NDC

Catalysts	**NDC**	**BNDC**	**PNDC**	**BPNDC**
Mass activity (mA/mg_{catal})	-2.6	-3.0	-5.4	-6.0

Calculated mass activities at 0.6V (*vs* RHE) for the prepared Catalysts and N-doped catalysts reported by other research group : N-doped carbon prepared by traditional methods (a to d, pyrolysis of C-N containing precursor) and by modified methods (e to g, secondary pyrolysis or use of sacrificial supports).

XRD results *of the prepared catalysts*

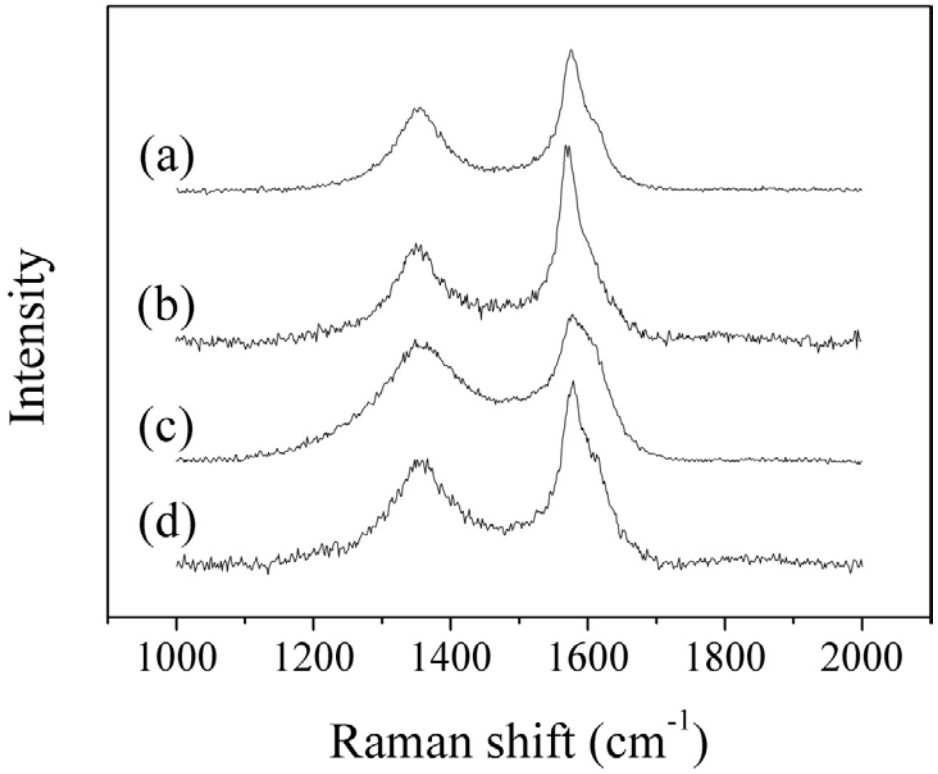


(a) NDC (b) BNDC
(c) PNDC (d) BPNDC

G(ooo) : graphite
● : Co
■ : Fe
▲ : Fe incorporated Co_2P

1. Graphite is synthesized.
2. Some metal residues (e.g. Co, Fe, or their alloy) are still remained after acid treatment → ∵graphite-encapsulation of metals prevent penetration of proton.
3. B-doping : Crystallinity of graphite ↑ (∵ sp^2 bonding, similar atomic size)
4. P-doping : Crystallinity of graphite ↓ (∵ sp^3 bonding, bigger atomic size)
5. Presence of P-source results in metal phosphide

Disorder of carbon structure confirmed by Raman



Raman spectroscopy of (a) NDC, (b) BNDC, (c) PNDC and (d) BPNDC

Catalysts	NDC	BNDC	PNDC	BPNDC
D-band[a]	1355.2	1353.7	1358.4	1358.4
G-band[a]	1578.5	1576.9	1586.3	1584.7
I_D/I_G[b]	0.67	0.60	0.83	0.68

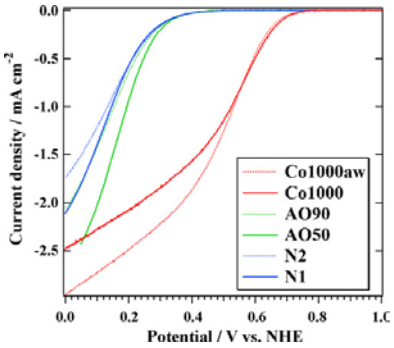
[a] cm^{-1}
[b] Intensity ratio of D- to G-band

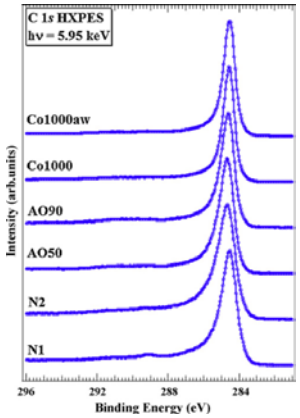
1. Graphite structure : D- and G-band is arisen at around 1355 cm^{-1} and 1580 cm^{-1}, respectively.
2. I_D/I_G : **BNDC < NDC < BPNDC < PNDC**
3. B-doping : Graphite structure ↑ (∵ sp^2 bonding, similar atomic size)
4. P-doping : Disorder ↑ (∵ sp^3 bonding, bigger atomic size)

Effects of B-doping as a function of ORR activity

1. order of graphite structure ↑

Niwa et al. reported that ORR activity of N-doped carbon was improved with increasing sp^2-carbon network.[1]

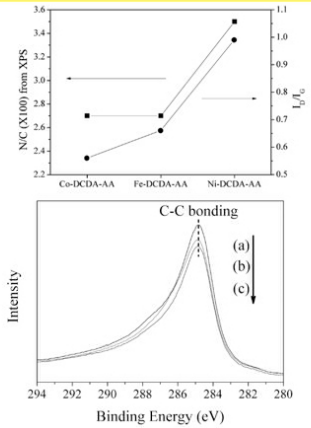




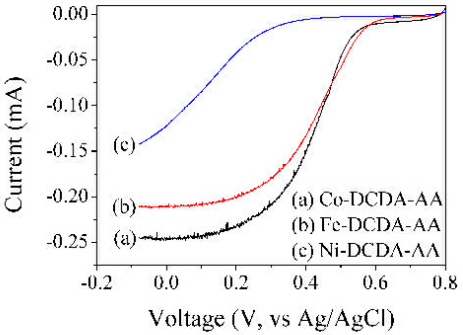
Our previous study also reported that degree of sp^2-carbon network is one of the major factors, determining ORR activity of N-doped carbon.[2]

Improvement of ORR activity as increasing sp^2-carbon network, is due to increment of electron conductivity.[3]

Degree of sp^2-carbon structure : Co->Fe->Ni-DCDA



ORR activity in acidic media : Co->Fe->Ni-DCDA



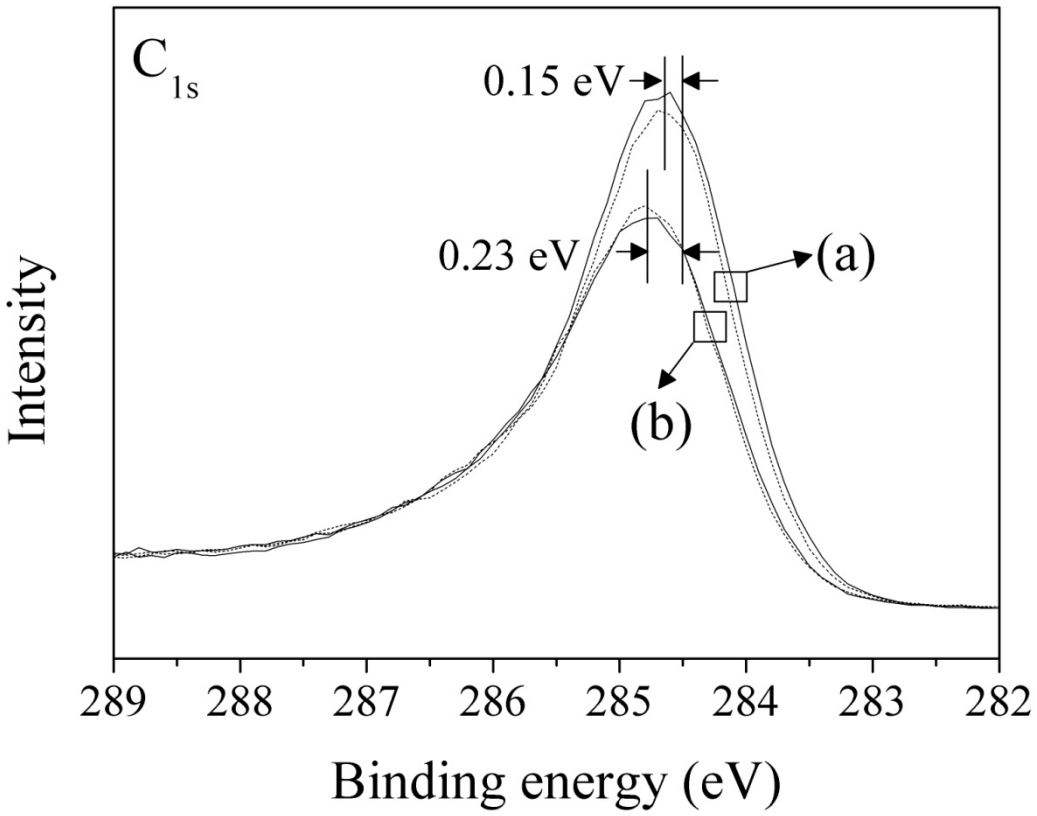
[1] Niwa et al./ JPS 196 (2011) 1006
[2] Choi et al./ Appl. Catal. B: Environment, under review
[3]Podyacheva et al./ Carbon 47 (2009) 1922

2. Amount of Pyridinic-N ↑

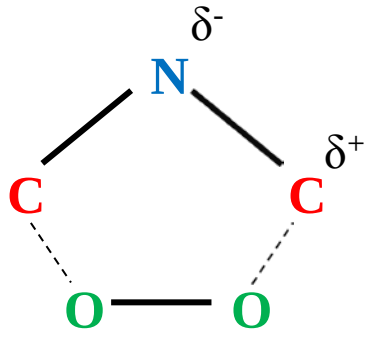
Order of activity according to the doping type of nitrogen :
Pyridinic > Graphitic > … > Pyridinic oxide

Dopant type	N-doping (%) N_1	N_2	N_3
NDC	44.1	45.1	10.8
BNDC	60.2	33.0	6.8
PNDC	53.6	38.7	7.7
BPNDC	63.8	31.5	4.7

XPS spectra of carbon (C_{1s}) in the catalysts



(a) NDC and BNDC
(b) PNDC and BPNDC

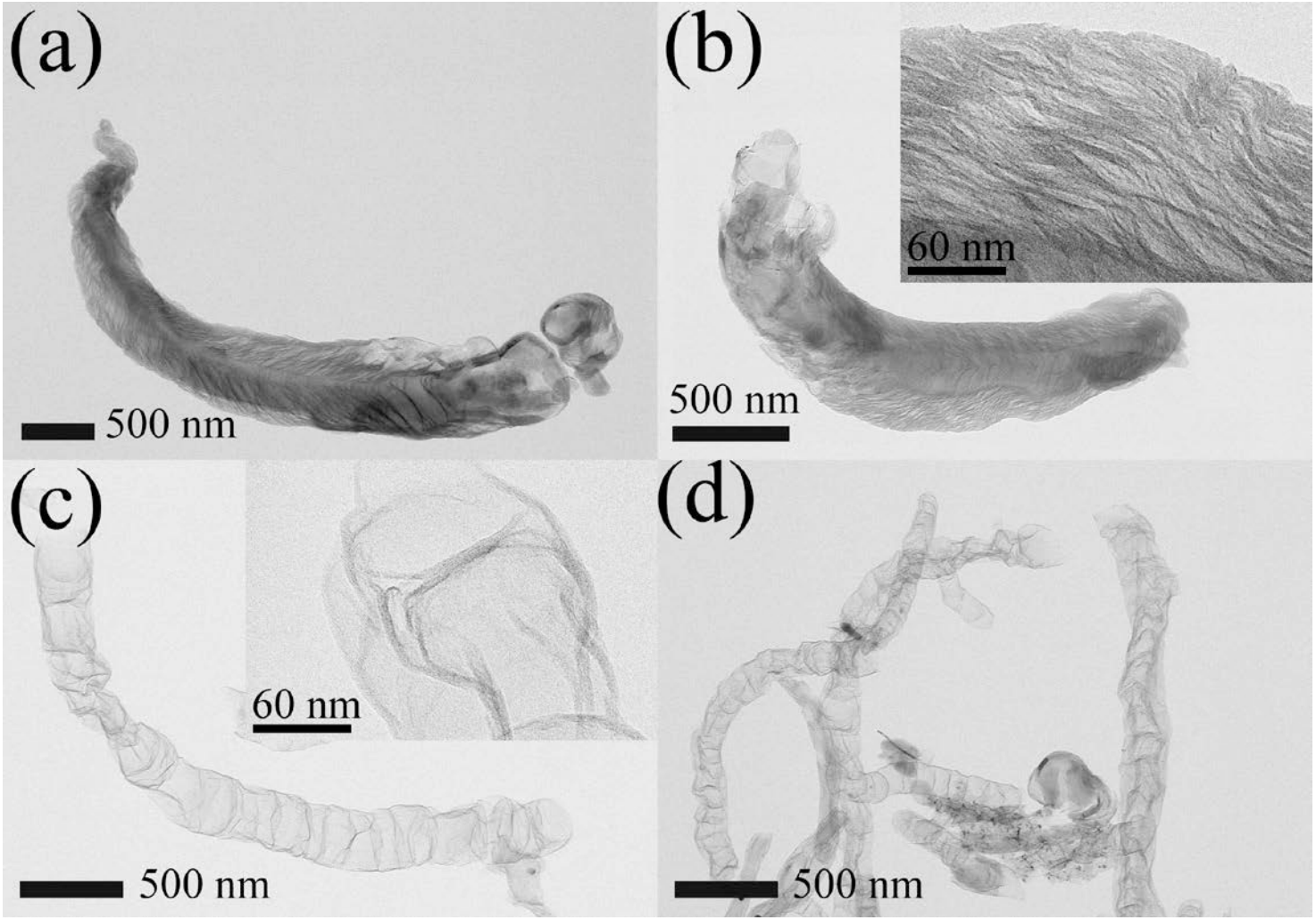


1. Binding energy of C-C bonding is up-shifted for
   NDC, BNDC : 0.15 eV
   PNDC, BPNDC : 0.23 eV

2. Up-shift of C-C binding energy is due to high electro-negativity of N atom.

3. In the case of incorporation of P atom, more electron delocalization from carbon atom are occurred rather than the case of N-doping, only.

TEM images *of the prepared catalysts*



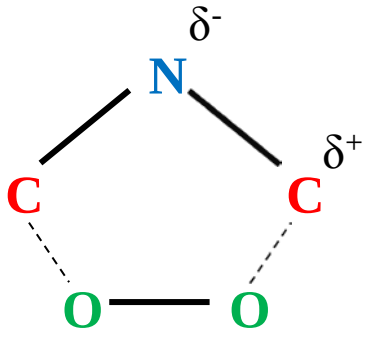
(a) NDC
(b) BNDC
(c) PNDC
(d) BPNDC

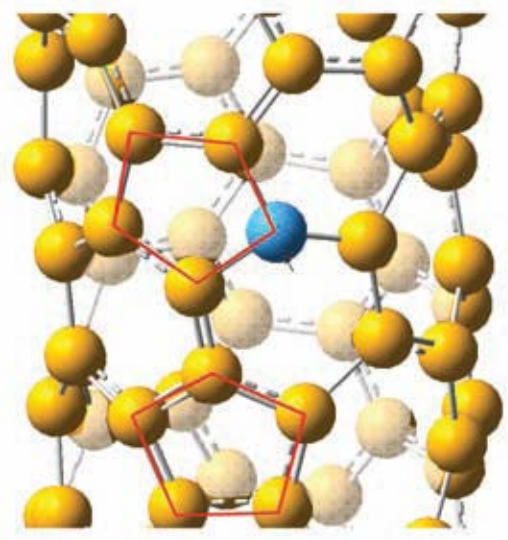
1. NDC and BNDC : Horn-like shape consisted of several carbon layers stacked up
2. PNDC and BPNDC : Bamboo-like CNTs consisted of many open edge sites

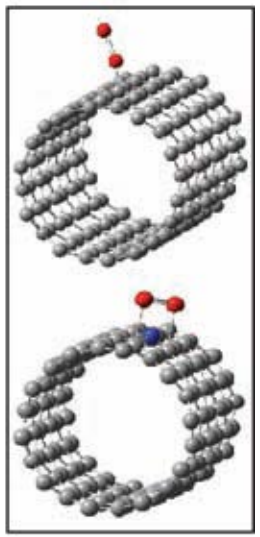
Effects of P-doping as a function of ORR activity

1. Enhanced charge delocalization

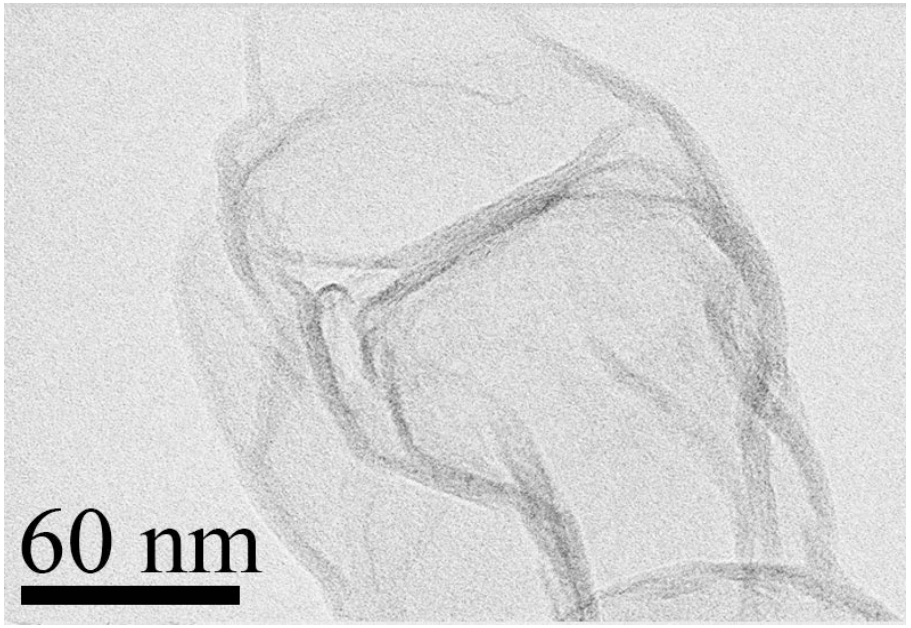
Gong et al. argued that ORR activity of N-doped carbon was arisen from adjacent carbon atoms, electron-delocalized by dopants.[1]

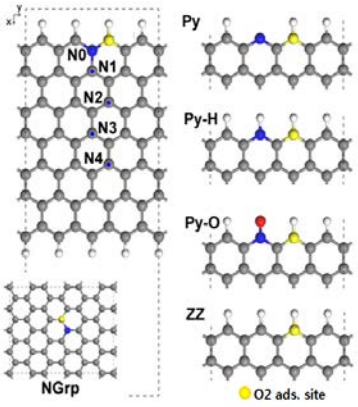






2. Production of edge sites





Many theoretical and experimental studies supports that edge sites doped by nitrogen have the highest ORR activity compared to other carbon sites.[2]

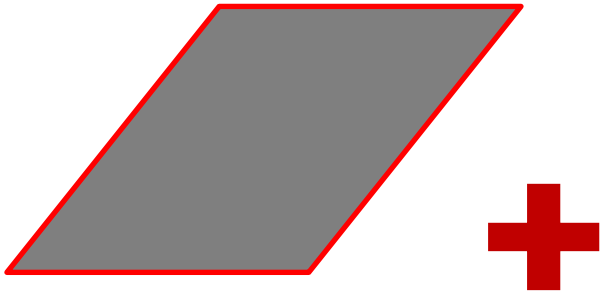
[1] Gong et al./ Science 323 (2009) 760
[2] Kim et al./ PCCP 13 (2011) 17505

Nitrogen-doped Graphene/Carbon Nanotube Self-Assembly for Efficient Oxygen Reduction Reaction in Acid Media

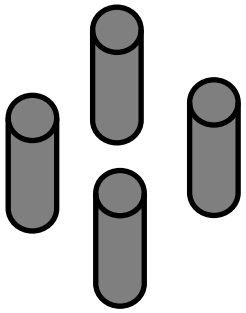
Appl. Catal. B: Environmental 144 (2013) 760-766

Experimental Strategy

Graphene



CNT

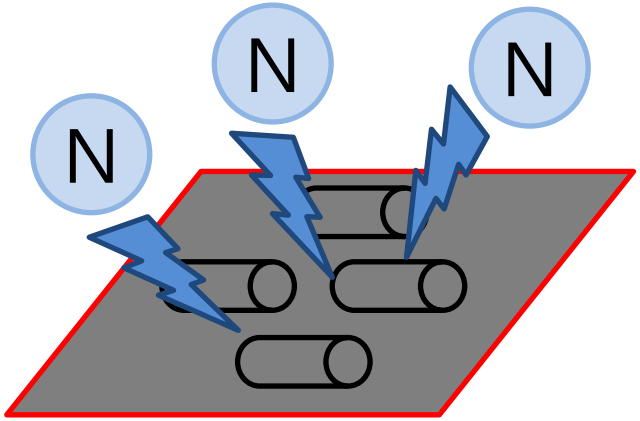


✓ Many edge sites
✓ Large surface area

✓ High conductivity

✓ Poor conductivity

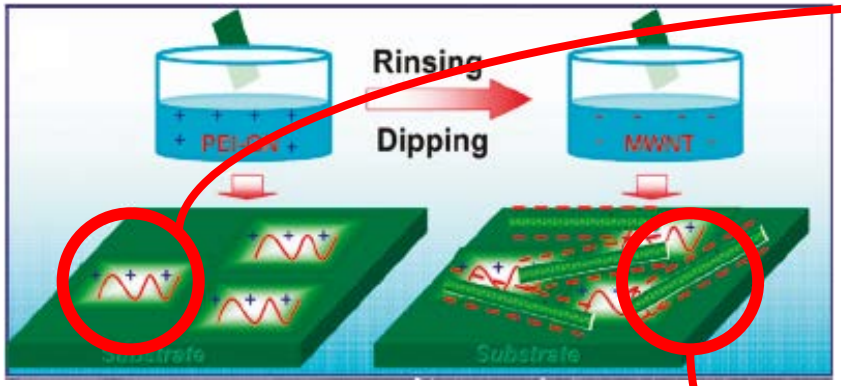
✓ Small surface area

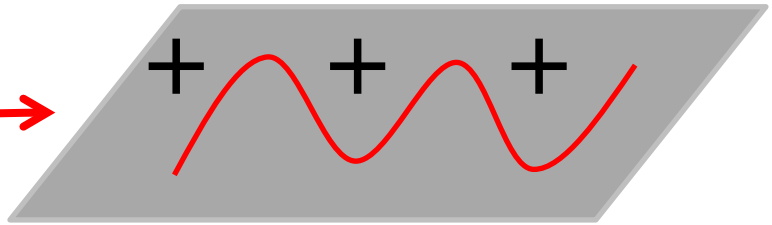


Additional N-doping for high ORR activity

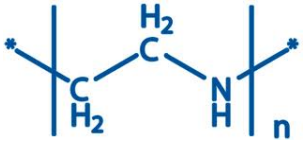
Experimental Strategy

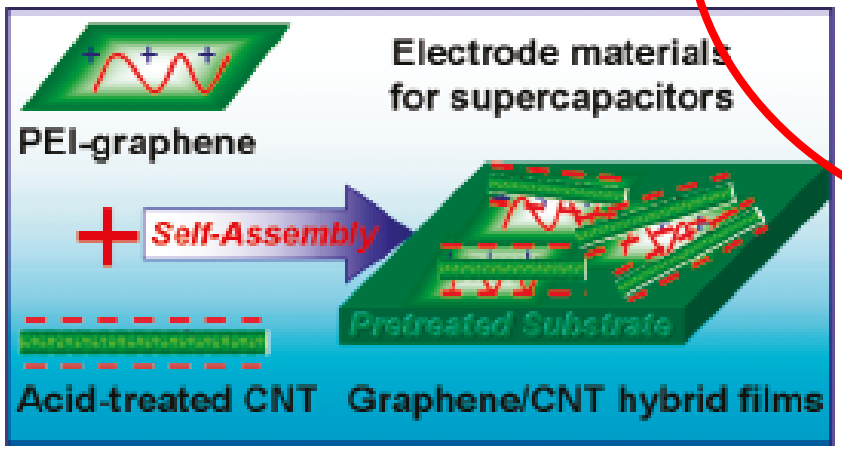
J. Phys. Chem. Lett, 2010, 1, 467-470





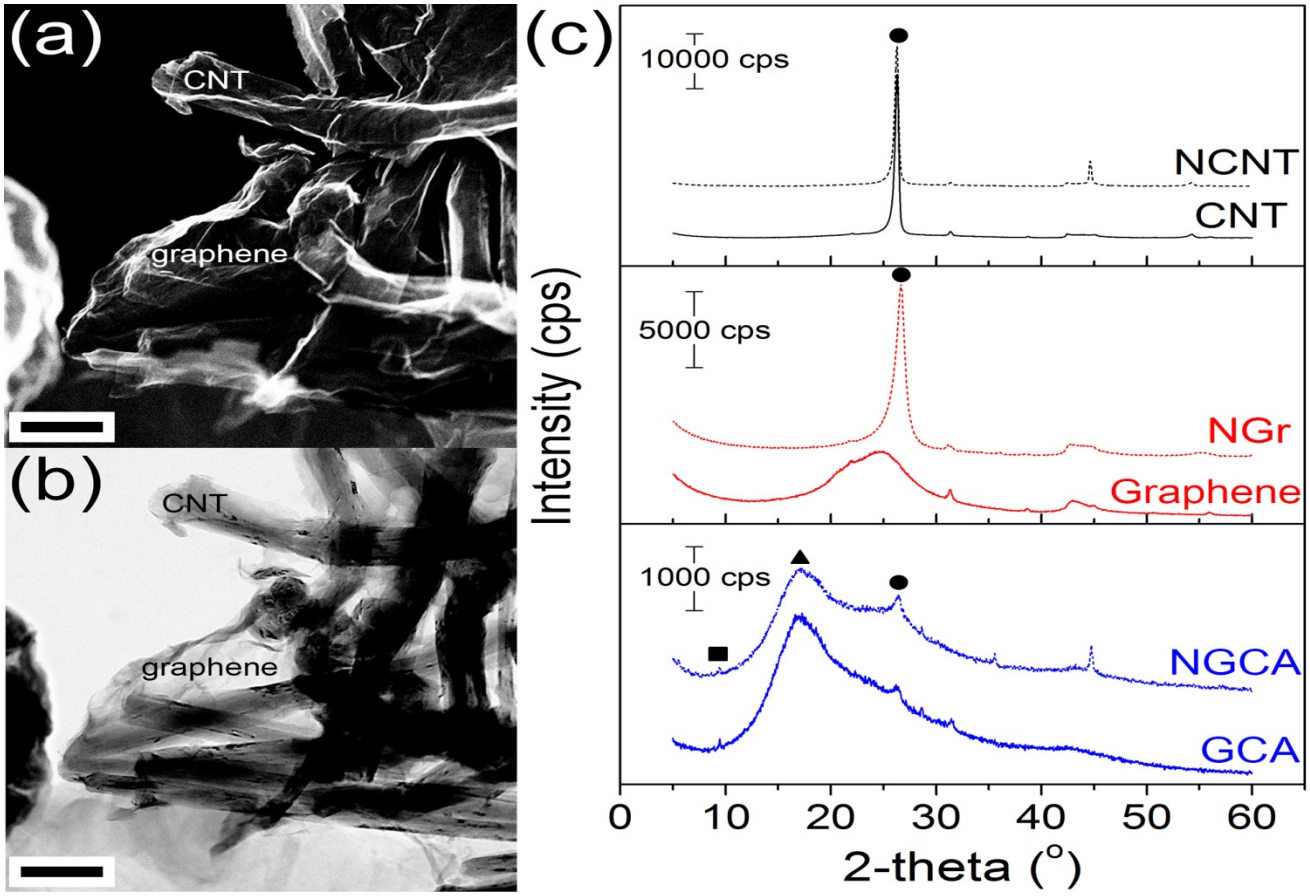
- ✓ Reducing GO with PEI
- ✓ PEI is positively carged
- ✓ PEI : poly(ethyleneimine)





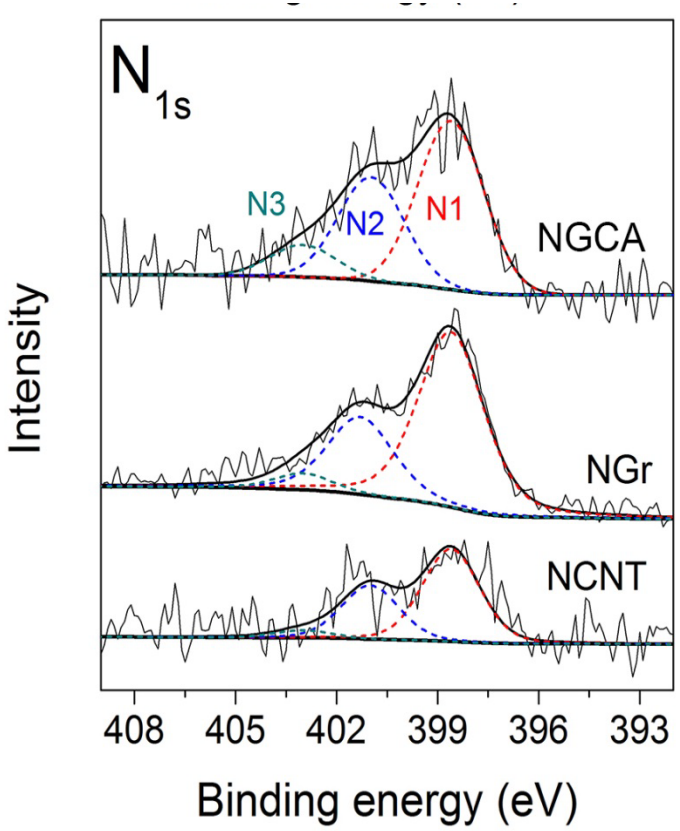
- ✓ Acid oxdized CNTs
- ✓ CNT is negatively charged

SEM, TEM, and XRD results of the prepared catalysts



- ✓ Graphene and CNT were successfully self-assembled
- ✓ CNT play a role as a spacer & an inhibitor in the restacking of graphene

XPS results of the prepared catalysts

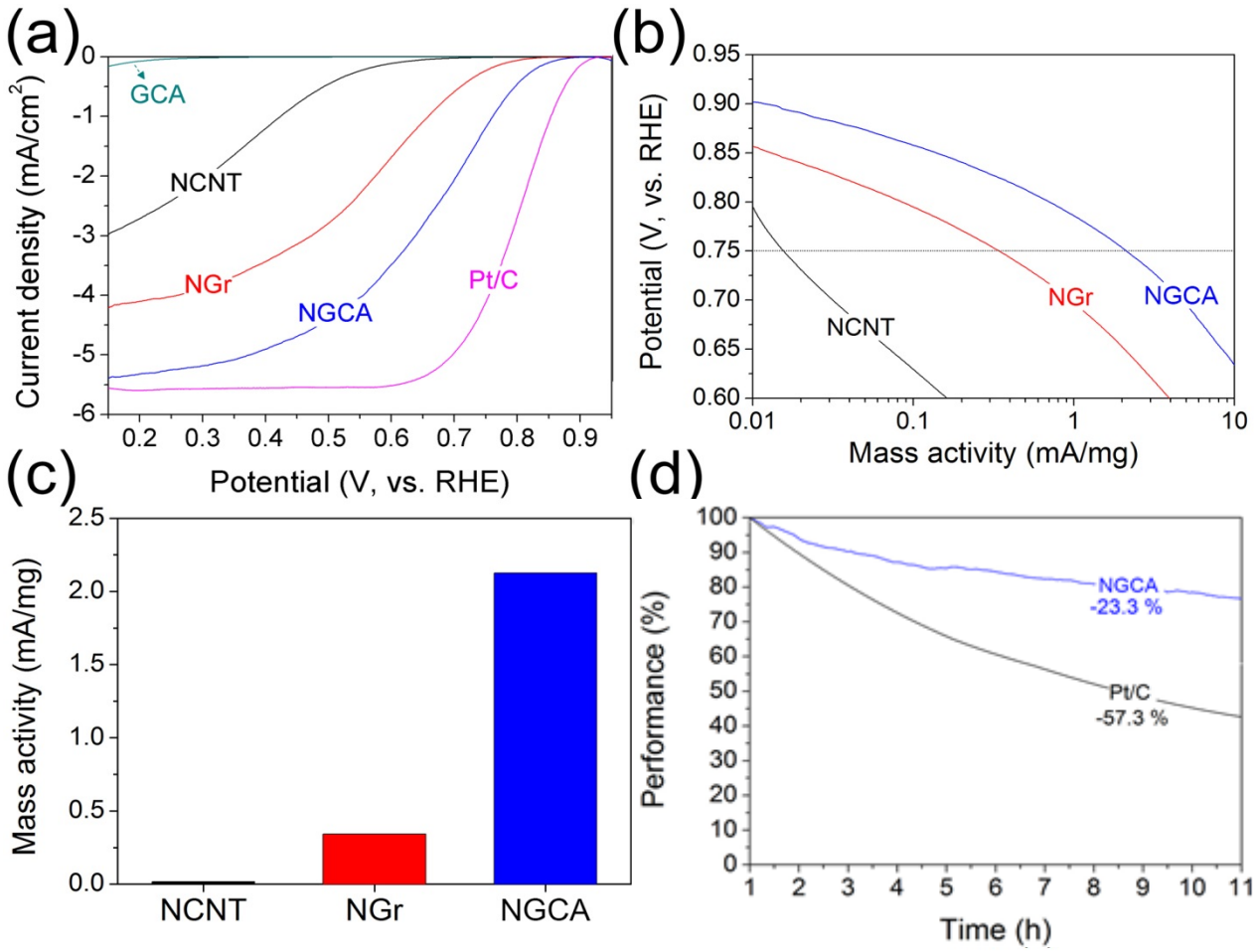


at.%		NCNT	NGr	NGCA
C		91.1	93.4	90.0
O		7.4	4.7	6.9
N		1.5	1.9	3.1
N-proportion(%)	N1	60.1	65.5	55.2
	N2	35.0	29.0	34.9
	N3	4.9	5.5	10.0

N1 : Pyridinic-N
N2 : Pyrrolic- or graphitic-N
N3 : Pyridinic-oxide

- ✓ Similar proportion of N-phases
- ✓ Pyridinic-N is the dominat site

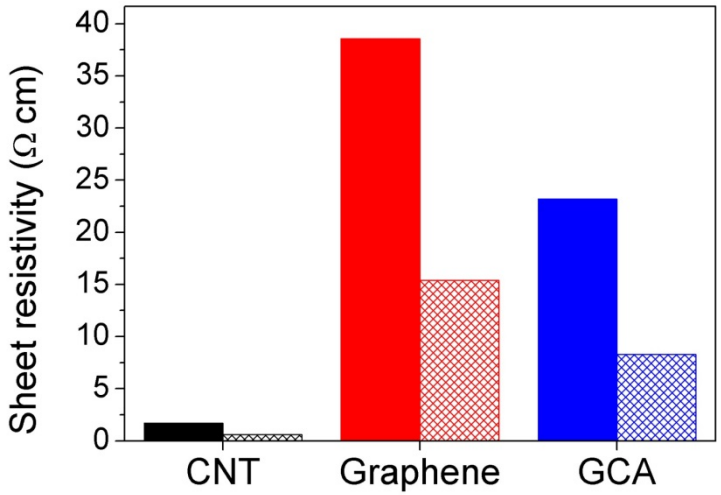
ORR performance of the prepared catalysts



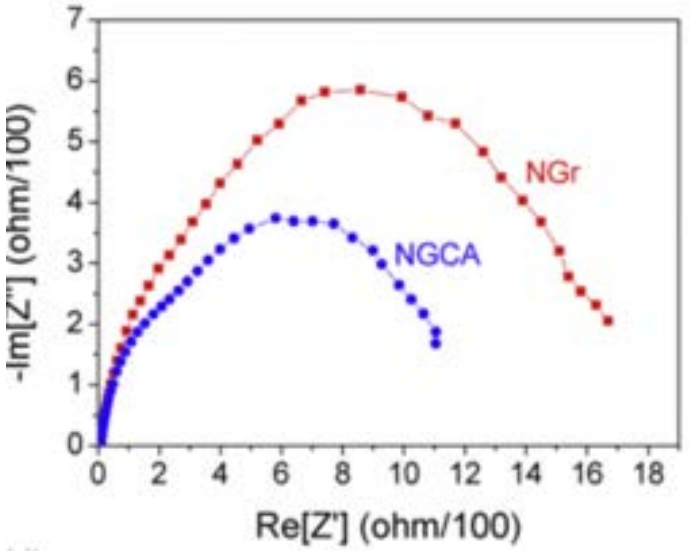
(a) LSV curves in O_2-bubbled 1M $HClO_4$ solutions with 2000rpm of electrode rpm
(b) Tafel-plots based on unit mass of the carbons
(c) mass activities (mA/mg) calculated at 0.75 V (*vs.* RHE)
(d) current-time chronoamperometric responses obtained at 0.6 V (*vs.* RHE) for 10h

- ✓ ~0.91 V (vs. RHE) of onset potential
- ✓ Six-fold higher mass activity than NGr (2.13mA/mg)
- ✓ Superior stability compared with Pt/C

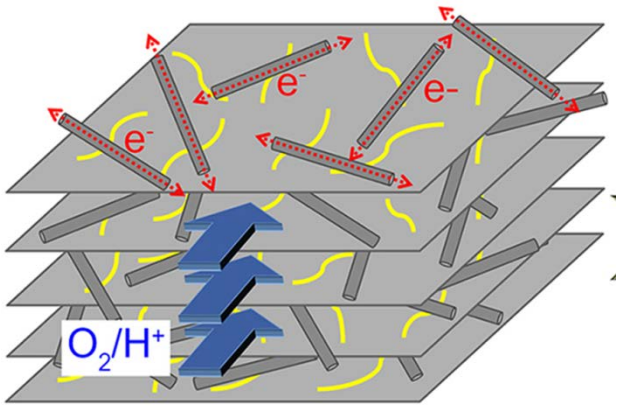
Resistance *of the prepared catalysts*



* Filled : before N-doping, Dashed : after N-doping



Graphene-CNT self-assembly

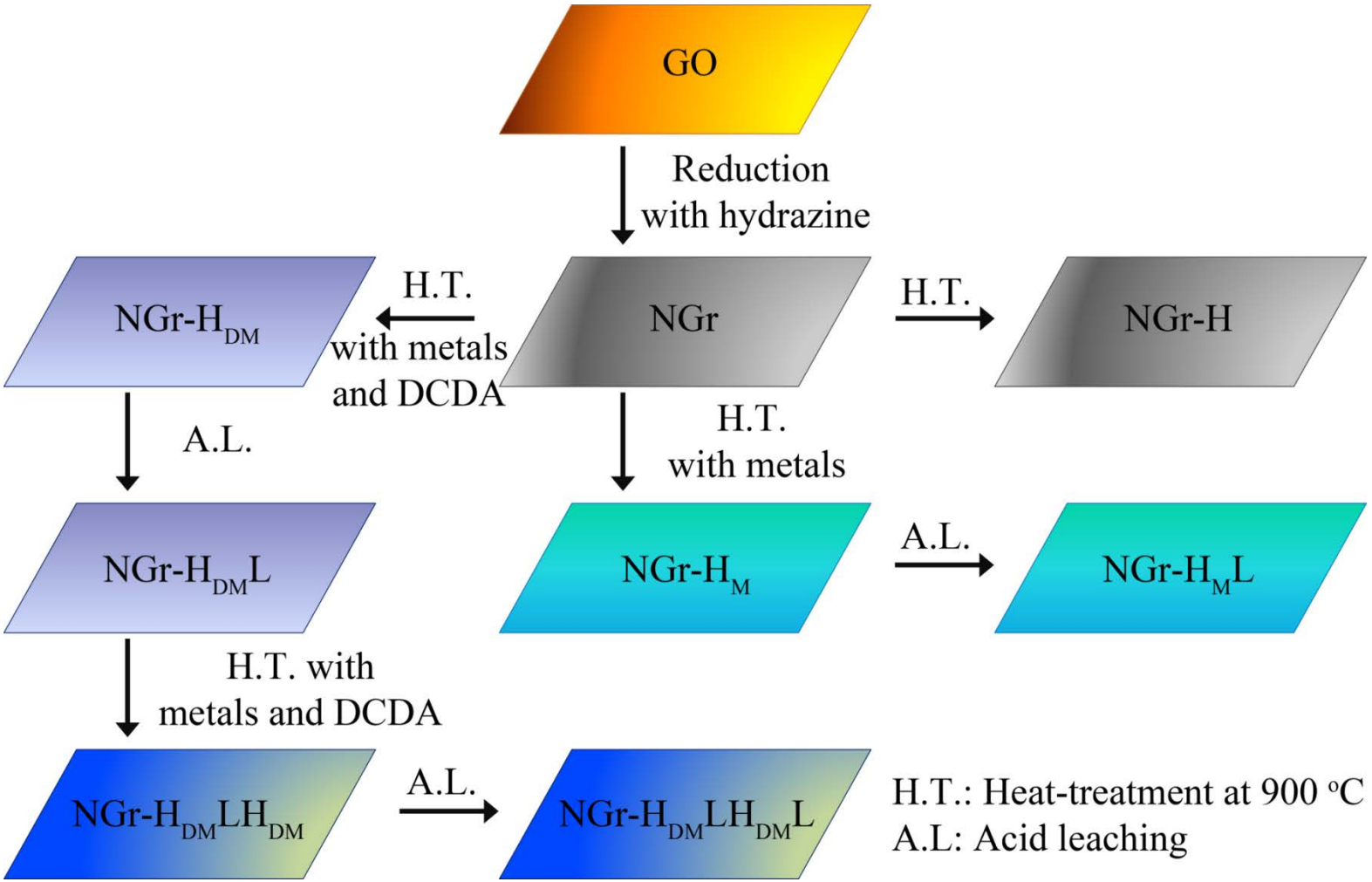


- ✓ Efficient transport of the reactant molecules due to the space between graphene layers
- ✓ Efficient transport of the electrons through the CNTs

Enhanced Electrochemical Oxygen Reduction Reaction by Restacking of N-doped Single Graphene Layers

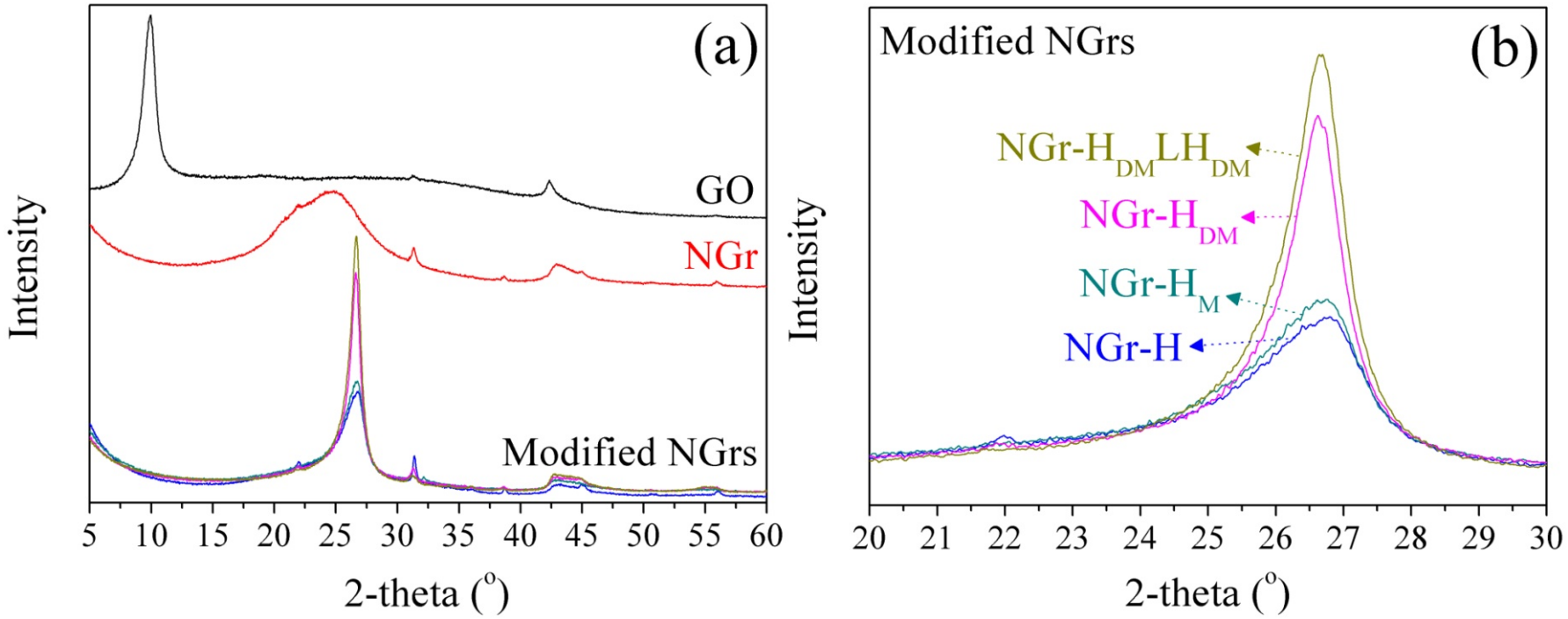
RSC Advances 3 (2013) 4246-4253

Preparation of the catalysts



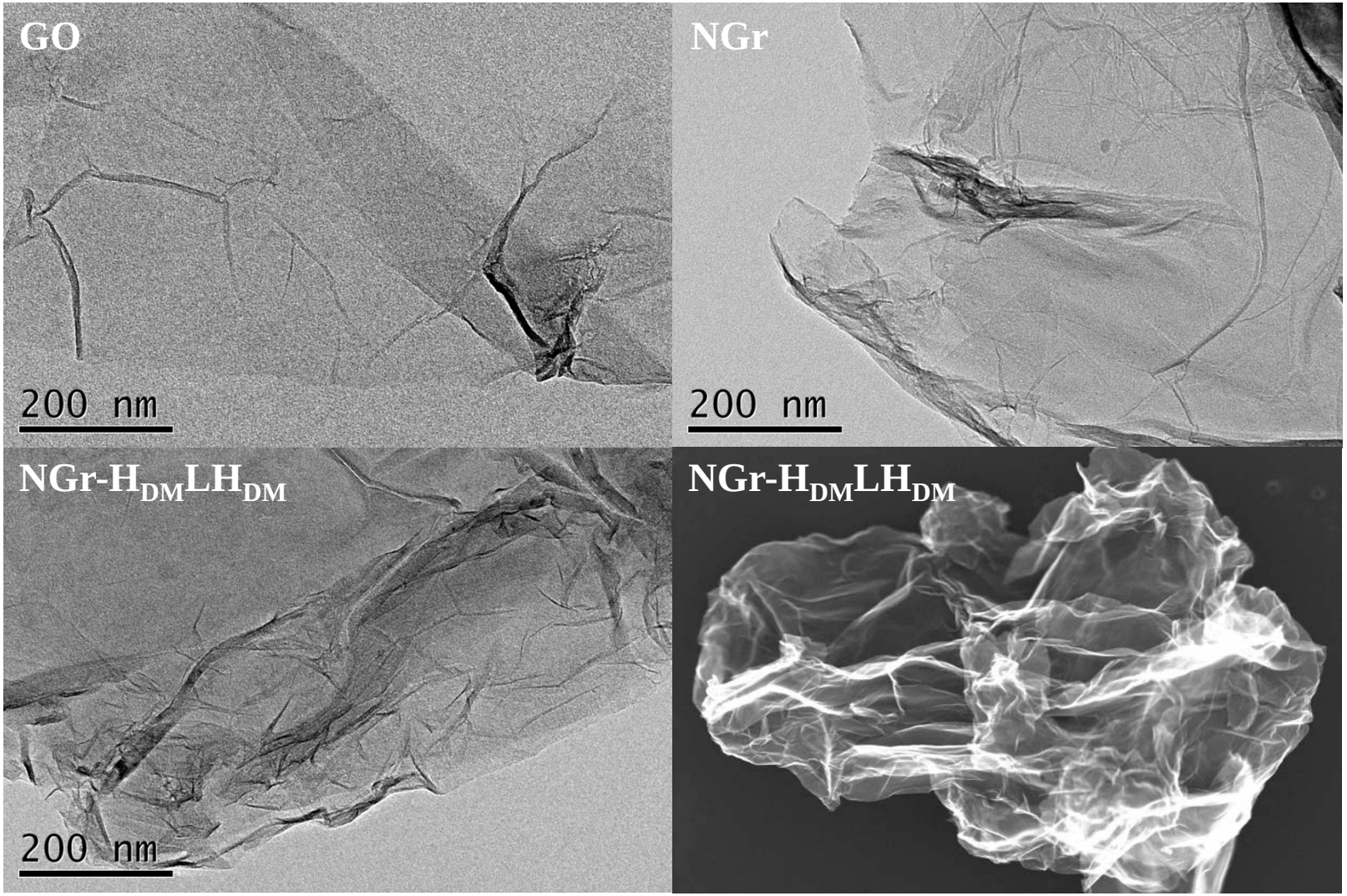
XRD results

(a) XRD patterns of the prepared catalysts and **(b) magnified XRD results** for modifies NGrs from 20° to 30° of 2-theta range.

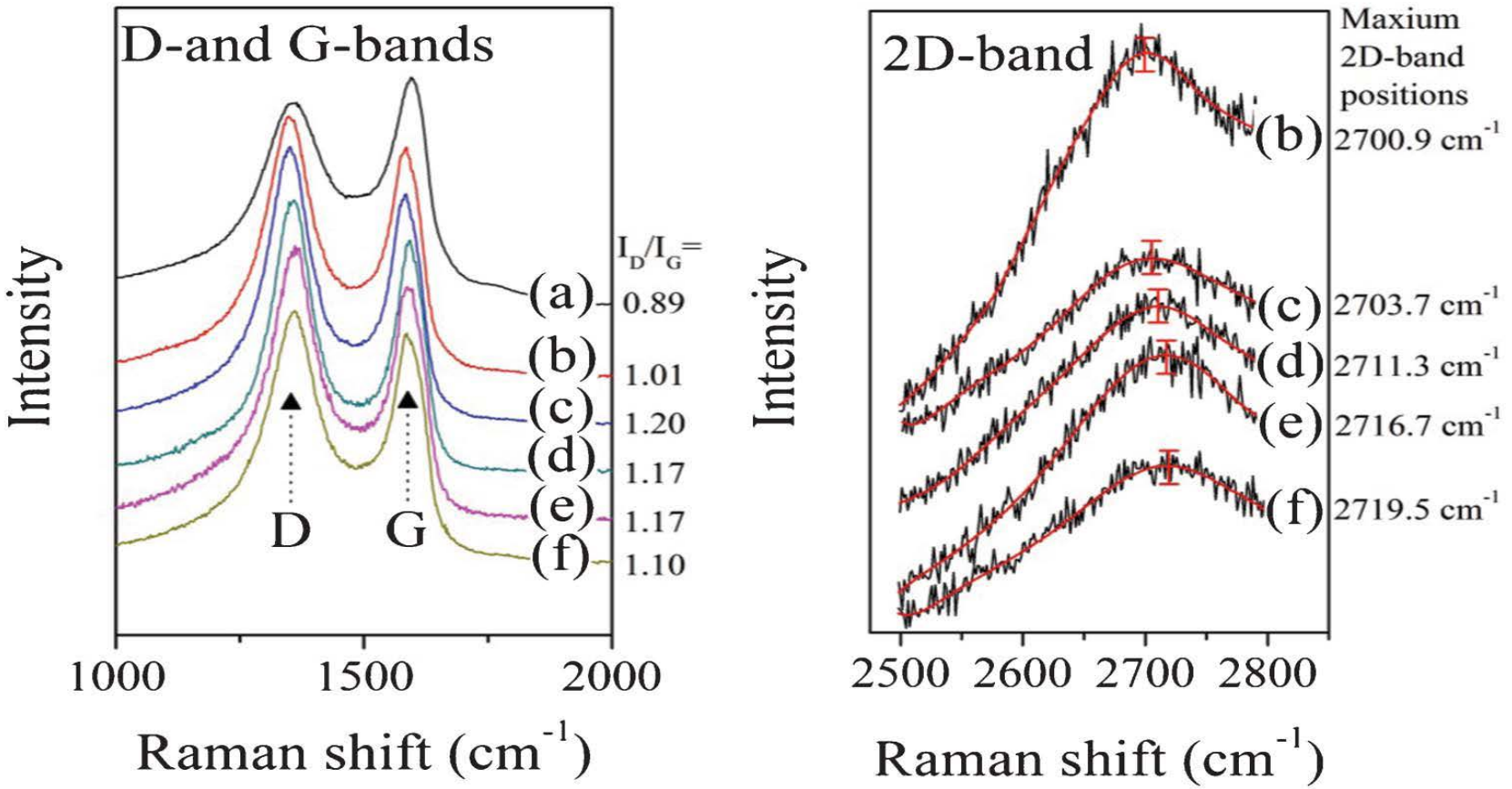


- ✓ Broaden XRD patterns → successful reduction of GO
- ✓ Crystallinity : NGr-H$_{DM}$LH$_{DM}$ > NGr-H$_{DM}$ > NGr-H$_{M}$ > NGr-H

TEM and SEM results



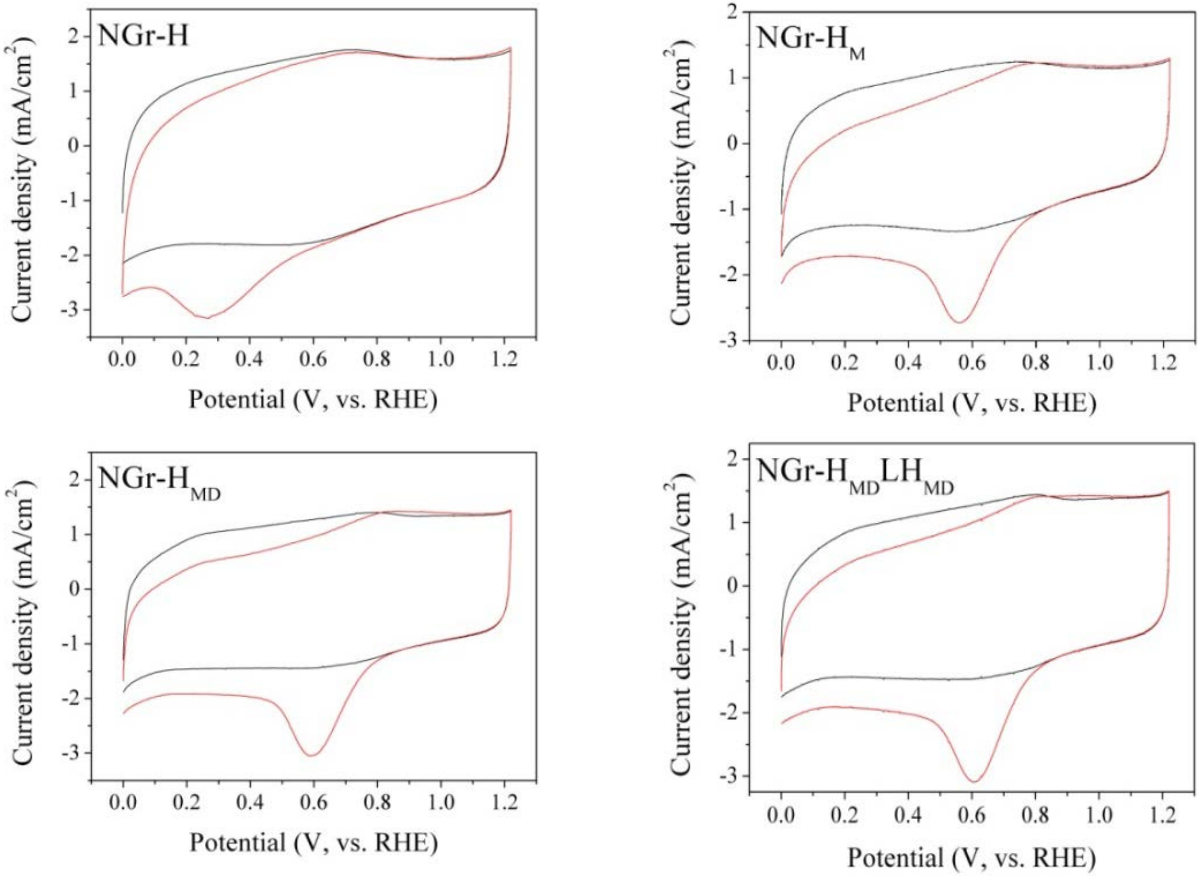
Raman Spectroscopy



(a) GO (b) NGr (c) NGr-H (d) NGr-H_M (e) NGr-H_{DM} (f) NGr-$H_{DM}LH_{DM}$

- ✓ High I_D/I_G ratio
- ✓ 2D-band position : between single layer graphene and graphite
  → restacking of graphene layer

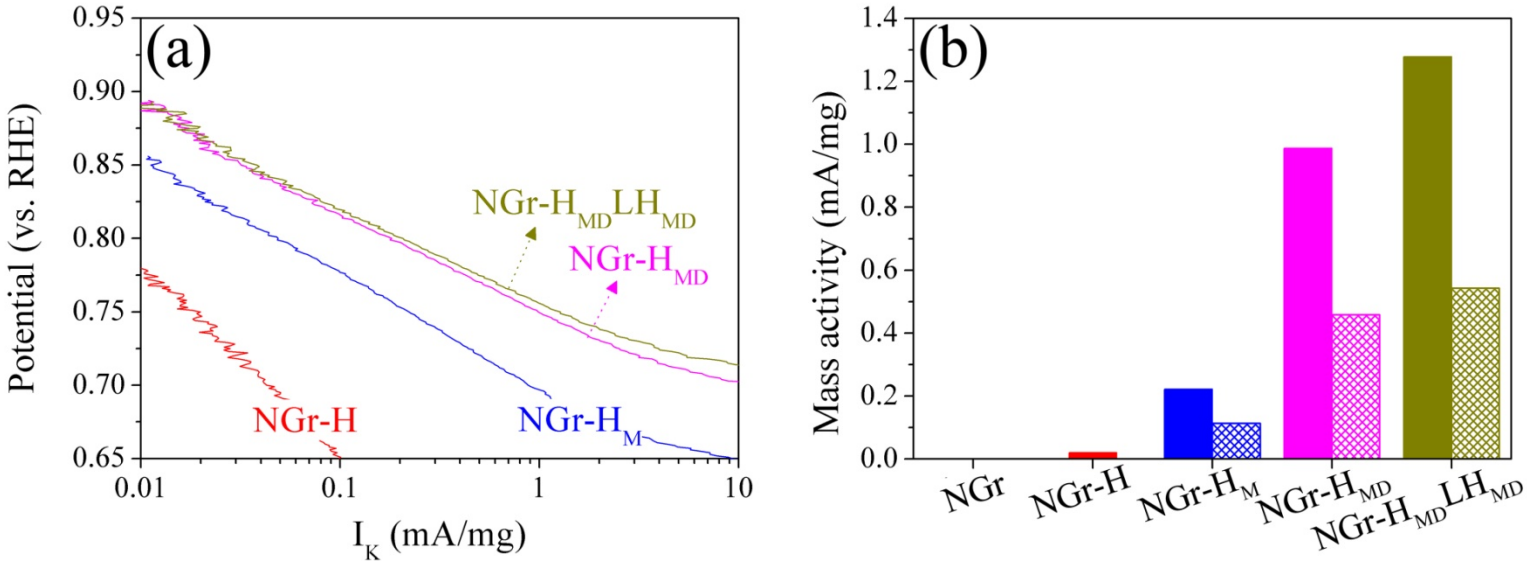
Performance of the prepared catalysts (1) - Cyclic Voltammetry (CV)



✓ High reduction peak potential ⇒ good ORR performance

✓ NGr-H$_{DM}$LH$_{DM}$ > NGr-H$_{DM}$ > NGr-H$_M$ > NGr

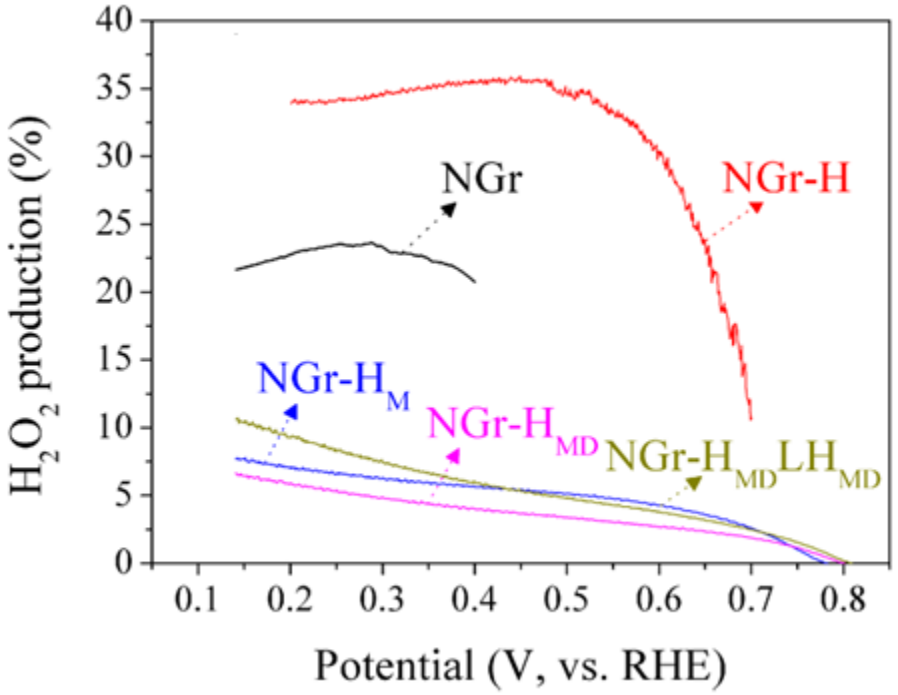
Performance of the prepared catalysts (2) - Tafel plot & Mass activity

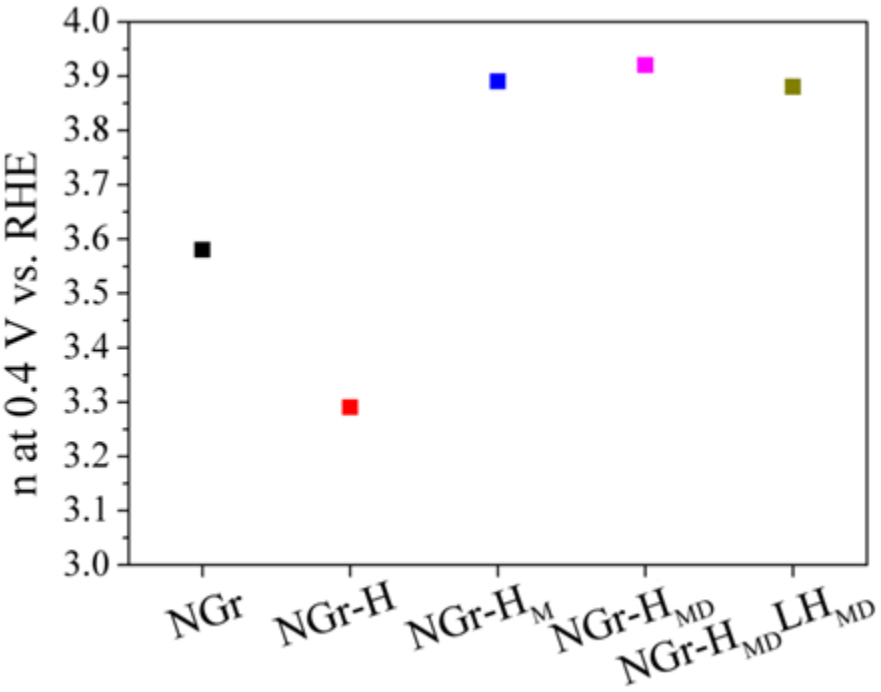


(a) Tafel plot of the prepared catalysts obtained from ORR results 1M $HClO_4$ electrolyte and (b) calculated mass activities at 0.75 V (vs. RHE)

	NGr	**NGr-H**	**NGr-H_M**	**NGr-H_{MD}**	**NGr-$H_{MD}LH_{MD}$**
Onset potential (V, vs. RHE)	0.58	0.77	0.86	0.89	0.89
Mass activity (mA/mg) at 0.75 V (vs. RHE)	0	0.02	0.22	0.99	1.28

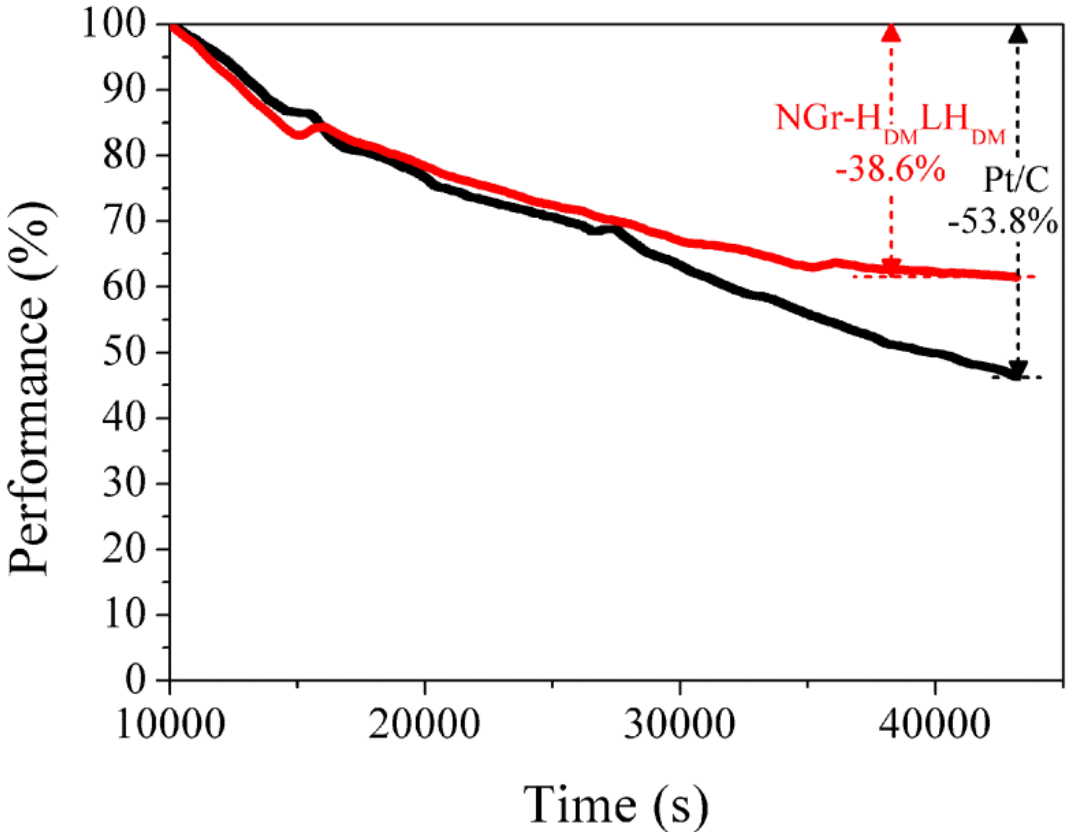
Performance of the prepared catalysts (3) – ORR pathway





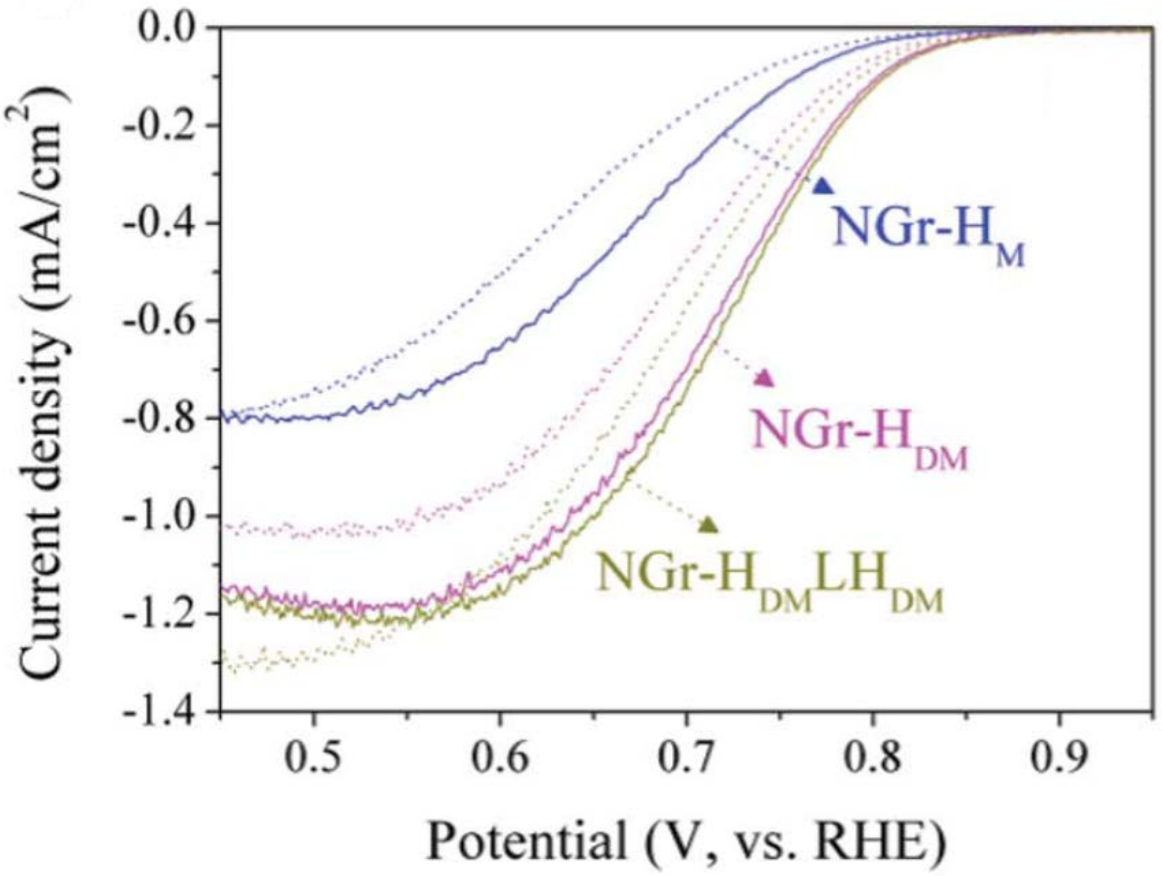
- ✓ Confirmed by RRDE measurement
- ✓ Near 4-electron transfer at 0.4V (vs. RHE)

Performance of the prepared catalysts (4) – Stability



- ✓ i-t chronoamperometry at 0.6V (vs. RHE) for 10h
- ✓ Outperformed stability compared with Pt/C

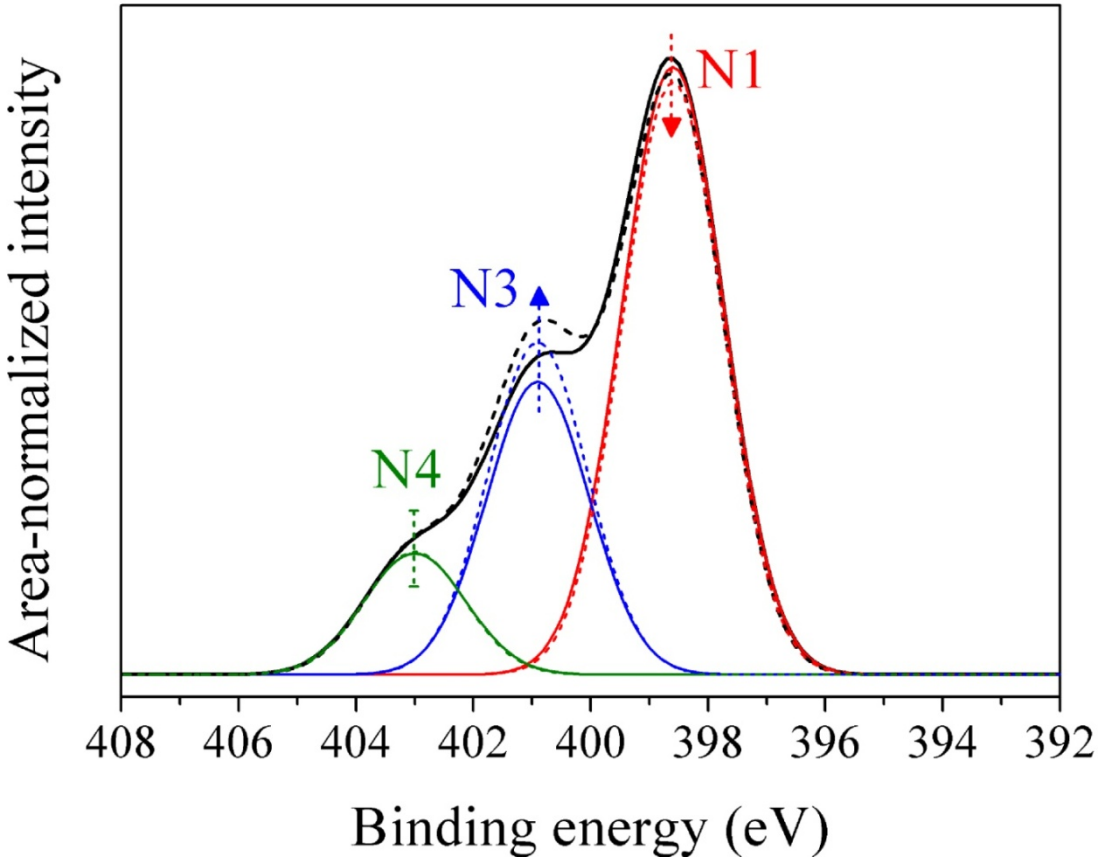
Acid leaching (1) - Linear Sweep Voltammetry Results



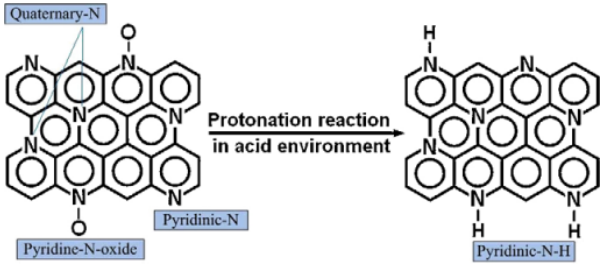
Dashed line : Acid leaching (O)
Solid line : Acid leaching (X)

✓ Performance decreased after acid leaching

Acid leaching (2) - XPS-N_{1s} Results



N1 : Pyridinic-N
N3 : Graphitic-N
N4 : Pyridinic-oxide



- ✓ Pyridinic-N sites decreased & graphitic-N sites increased
- ✓ Pyridinic-N ⇒ Pyridinic-N-H (protonation)
- ✓ Pyridinic-N-H has similar binding energy with graphitic-N

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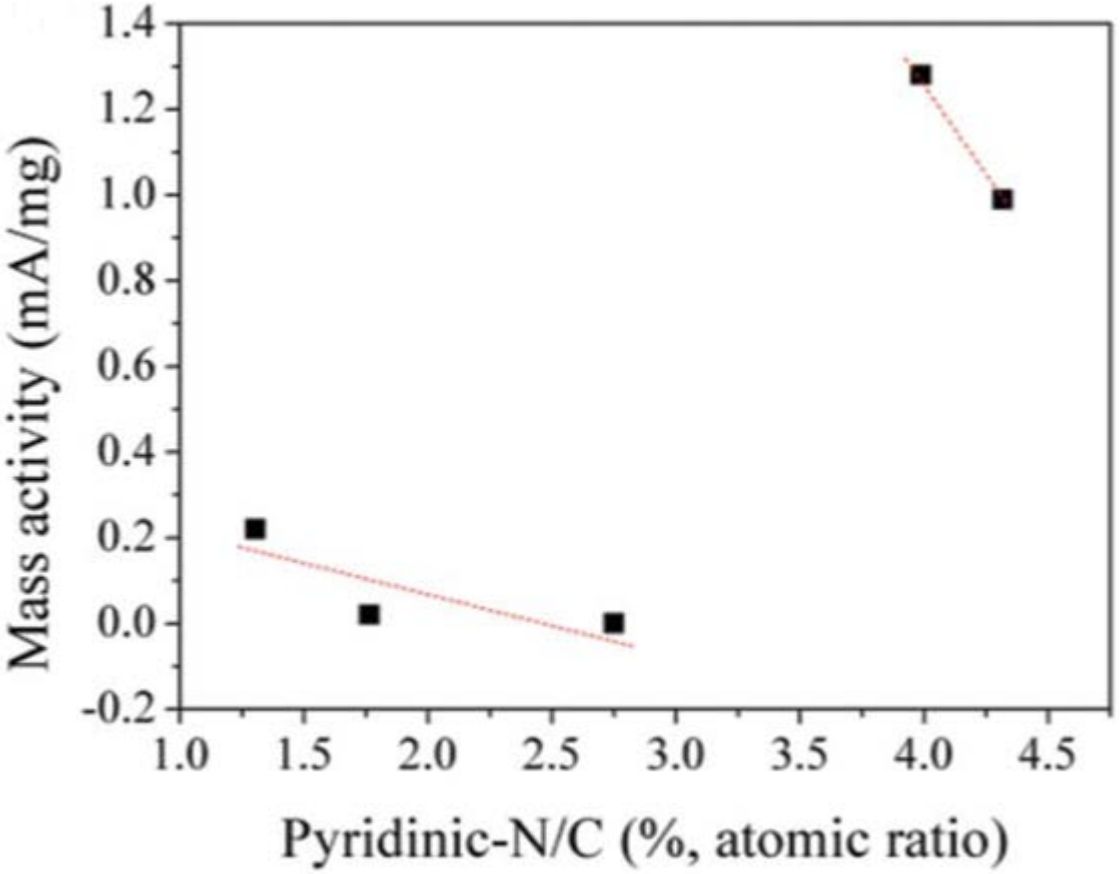
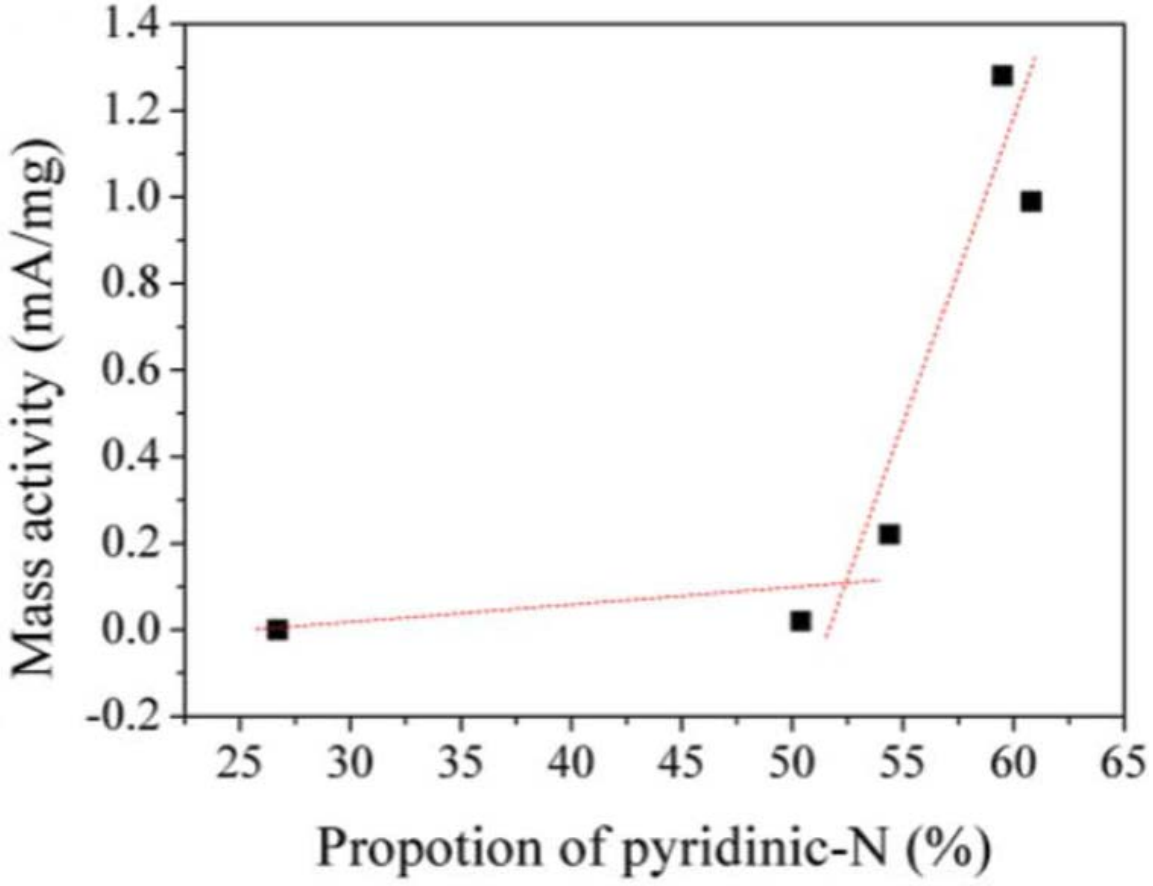
Restacking of the graphene layers (1) – correlated factors



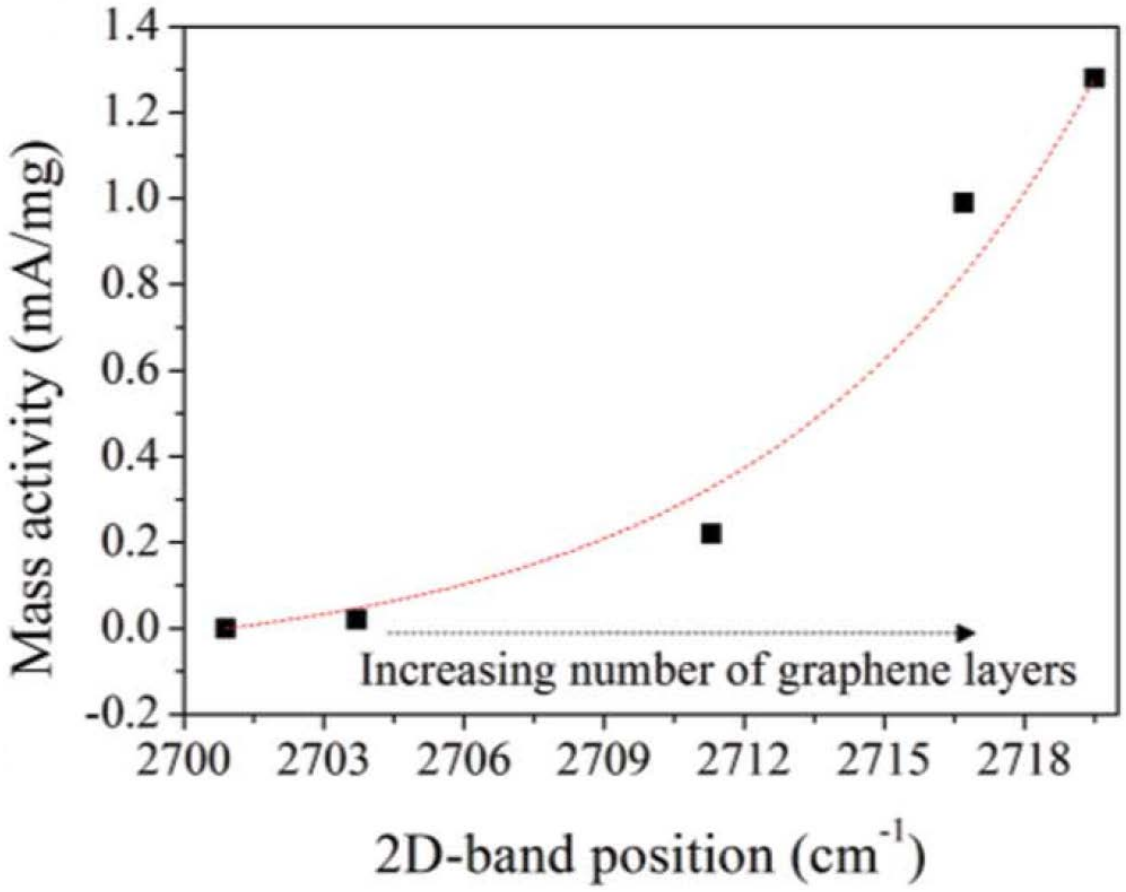
- ✓ Concentration of the pyridinic-N vs. Mass activity
- ✓ No clear correlation ⇒ Not an important factor

Restacking of the graphene layers (2) – correlated factors



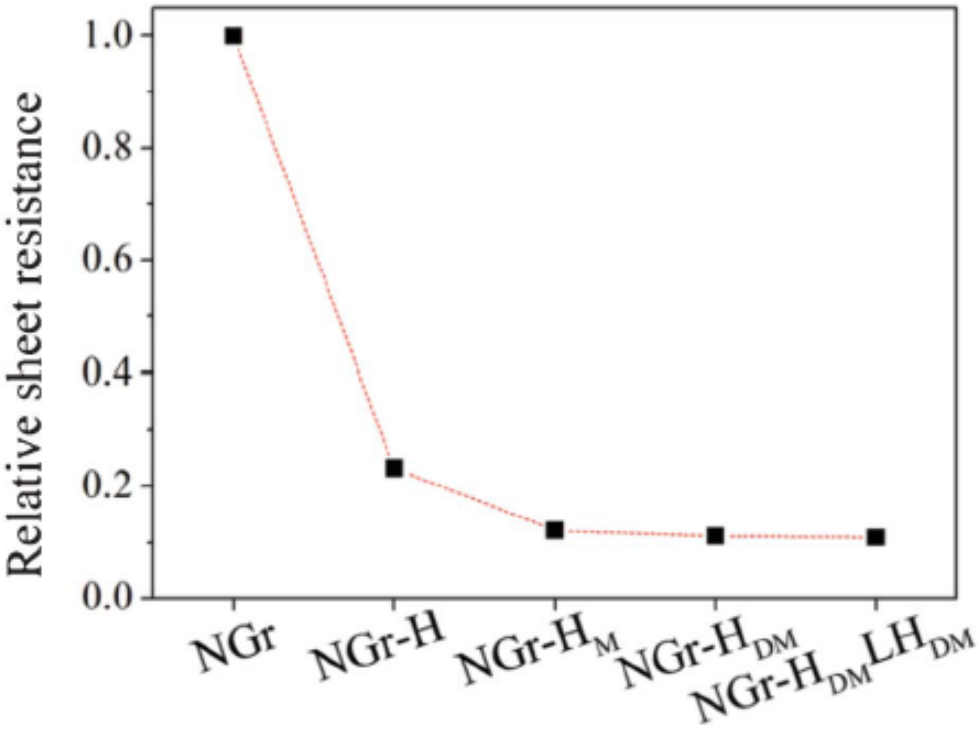
- ✓ Proportion of the pyridinic-N vs. Mass activity
- ✓ One factor of the ORR performance
- ✓ Not very clear

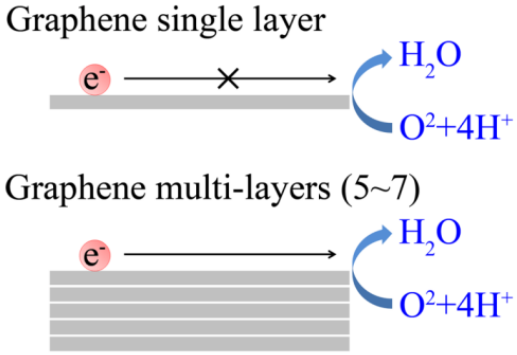
Restacking of the graphene layers (3) – correlated factors



- ✓ **Number of graphene layers** vs. Mass activity
- ✓ Crucial factor of the ORR performance
- ✓ Number of layers increased ⇒ Performance increased

Sheet resistance of the prepared catalysts



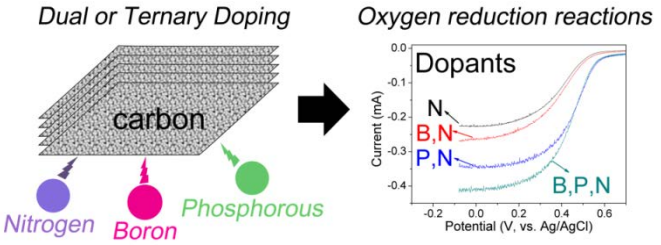


✓ Stacked graphene layers
⇒ Lower sheet resistance
⇒ Induce facile electron transfer
⇒ Desirable in ORR

Conclusion

Carbon

Heteroatom doping



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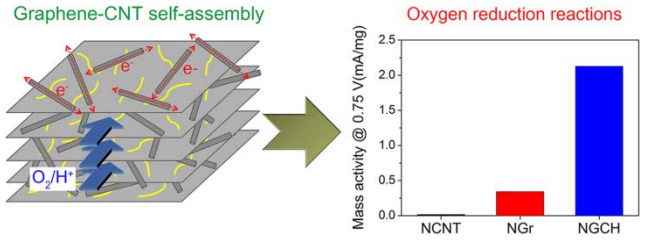
Morphological modification



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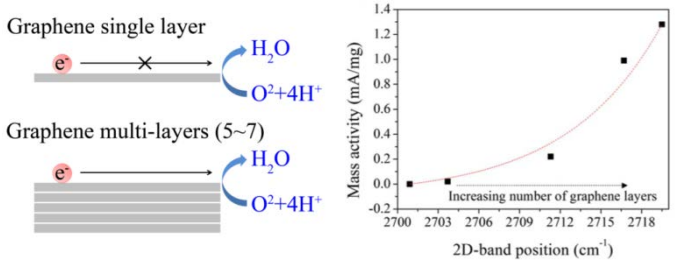
Graphene



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