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Enhancing the rate capability of nanomaterials as lithium ion battaery electrodes by tuning their structure

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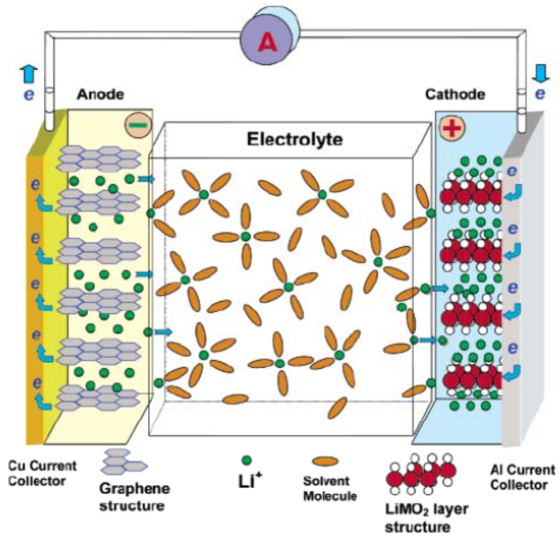
Dynamic LIBs for EVs

- The development of LIBs
  - High energy
  - High power
  - Safety

Key issues →

- The electrodes
  - High capacity
  - High rate capability
  - Intelligent prevention



The strategies of designing electrode materials of high performances

- New compounds and new reactions
- Nanosized materials
- Structure tuning

→

- Multi-electron transferring
- High specific surface and short Li^+ transportation path
- Tuning the rate of Li^+ reactions

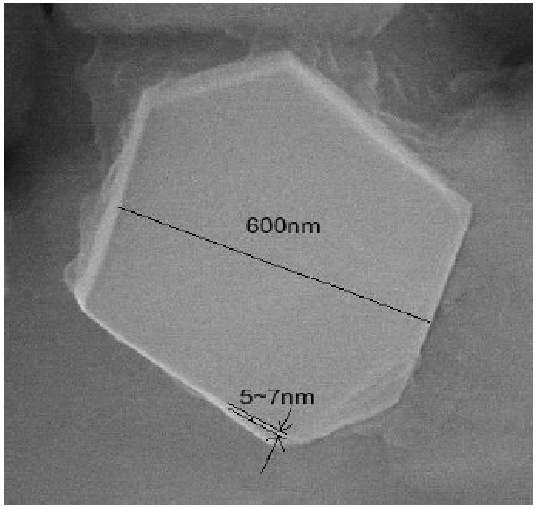
Outline

- **LNMO cathode**
- **LNCM cathode**
- **Co_3O_4 anode**

1. Lithium Mn-rich metal oxides (LNMO) nanomaterials for lithium ion battery

- Habit-tuned LNMO nanoplates of high surface energy and high rate-capability

LNMO $Li[Li_{1/3-2x/3}M_xMn_{2/3-x/3}]O_2$ (M = Ni, Co, or/and Cr) nanoplates

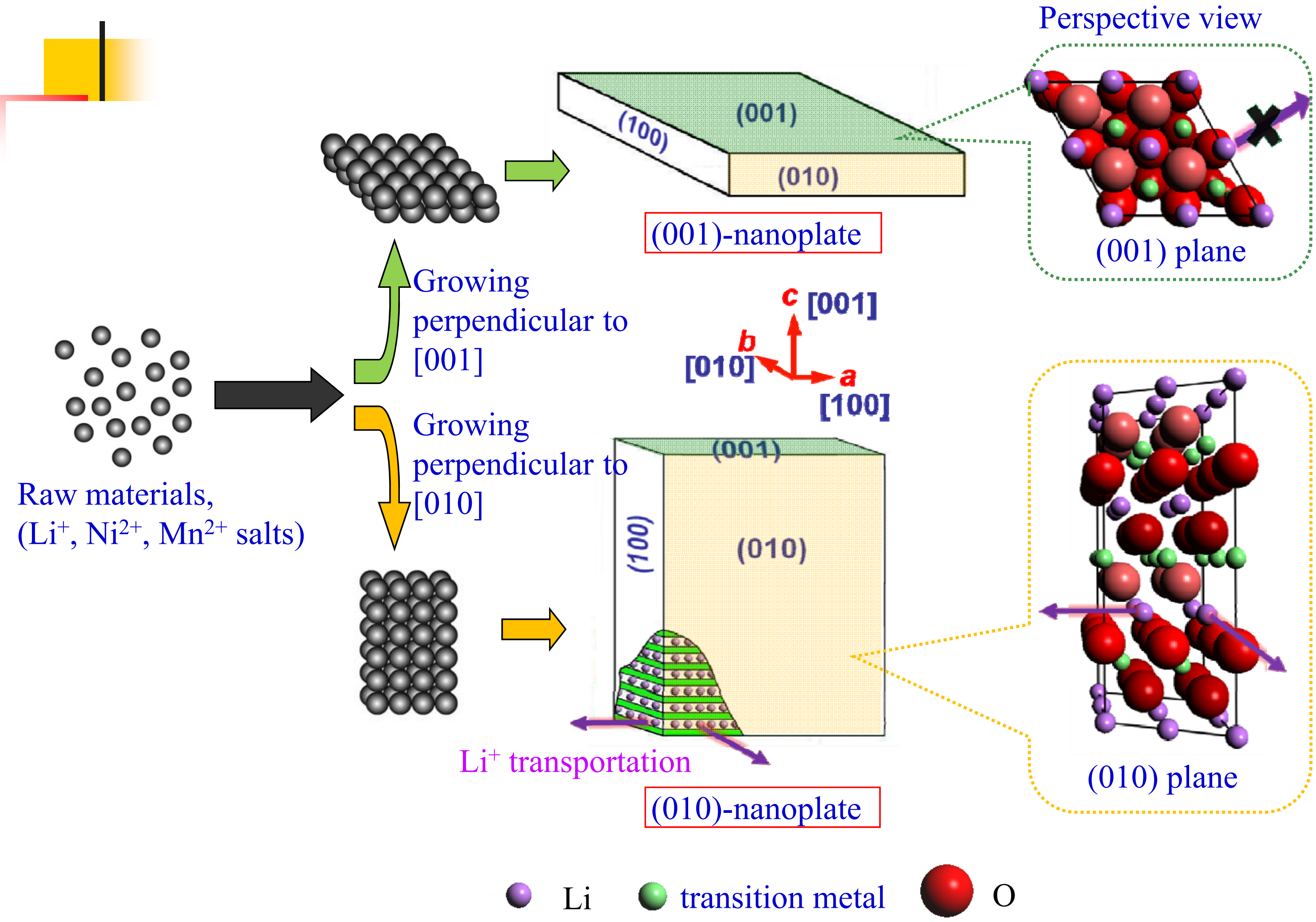


Li-Ni-Mn-O nanoplate

Lithium Mn-rich metal oxides such as $Li[Li_{1/3-2x/3}M_xMn_{2/3-x/3}]O_2$ (M = Ni, Co, or/and Cr) are currently used as up-to-date cathode materials for LIBs owing to their high capacity of over 200 mA h g^{-1} when charged to 4.5 V or higher.

However, the $Li[Li_{1/3-2x/3}M_xMn_{2/3-x/3}]O_2$ (LNMO) materials exists a rapidly fading capacity and a poor rate-capability.

LNMO nanoplates and their surface structure

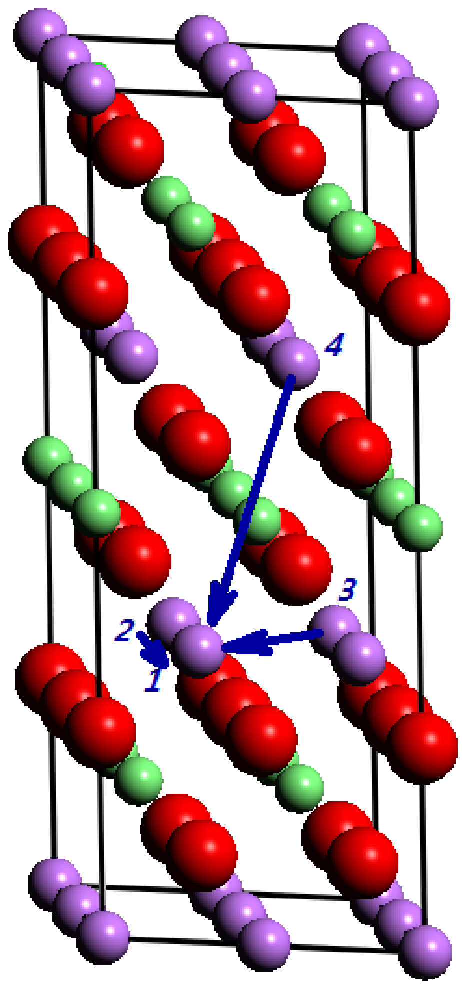


Surface energy calculation

Plane	Surface energy / J m^{-2}	Energy of Li-intercalation / meV	
(001)	0.937	2280	4->1
(010)	1.467	230	2->1
(110)	1.808	263	3->1

- The (001)-nanoplates are thermodynamic equilibrium products in most synthesis route when the synthesis reaction is under hydrothermal condition for a long enough time

- The (010) (or (100)) plane that is perpendicular to the (001) plane is an active plane for Li+ deintercalation/intercalation

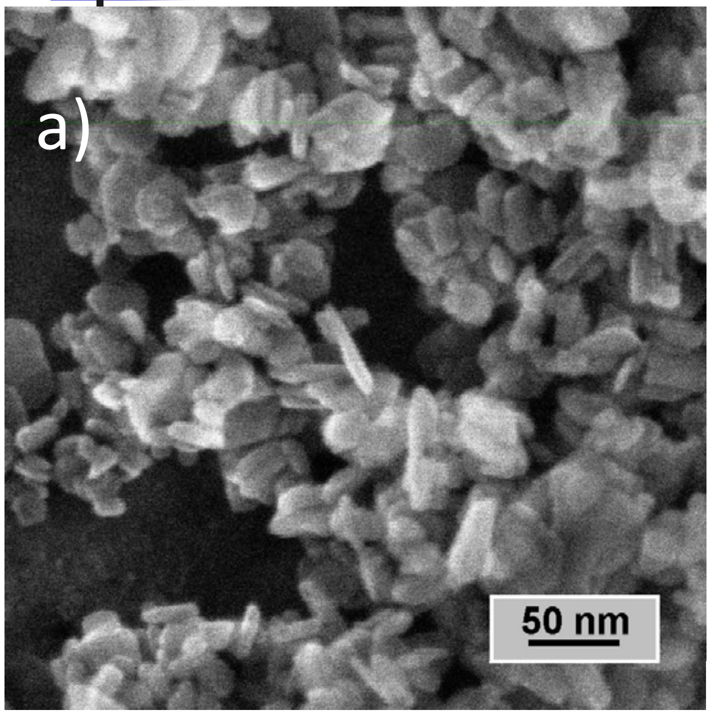


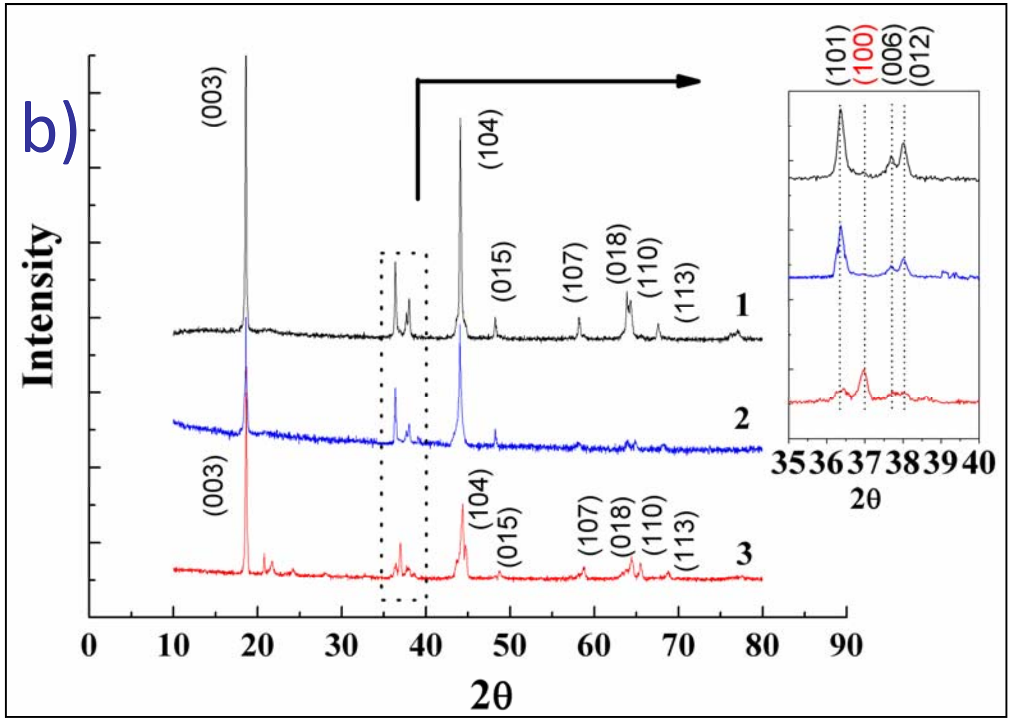
SEM & XRD

$Li[Li_{1/3-2x/3}Ni_xMn_{2/3-x/3}]O_2$

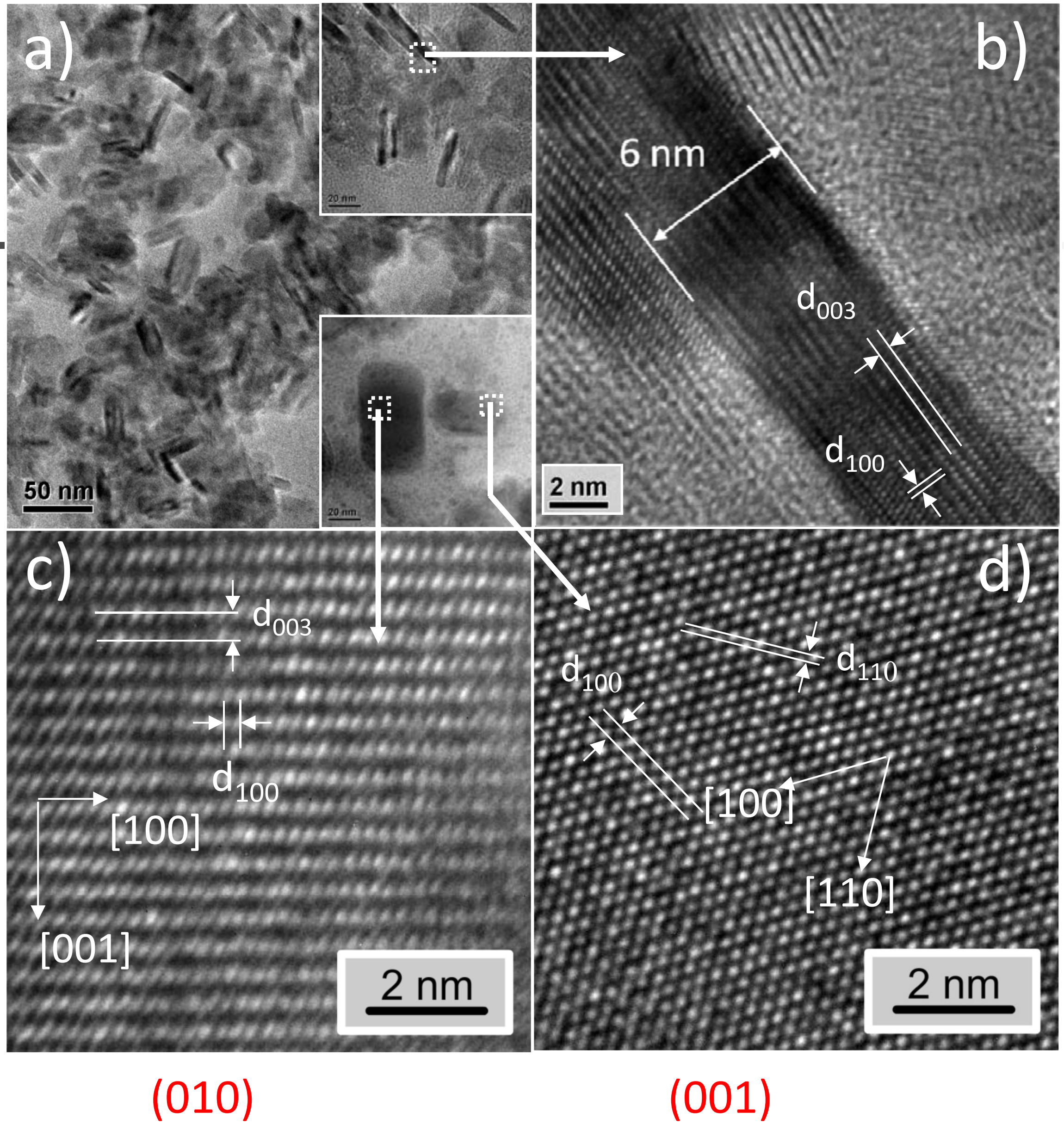
1. Particles
2. Conventional nanoplates (CN)
3. Habit-tuned nanoplates (HTN)

HTN

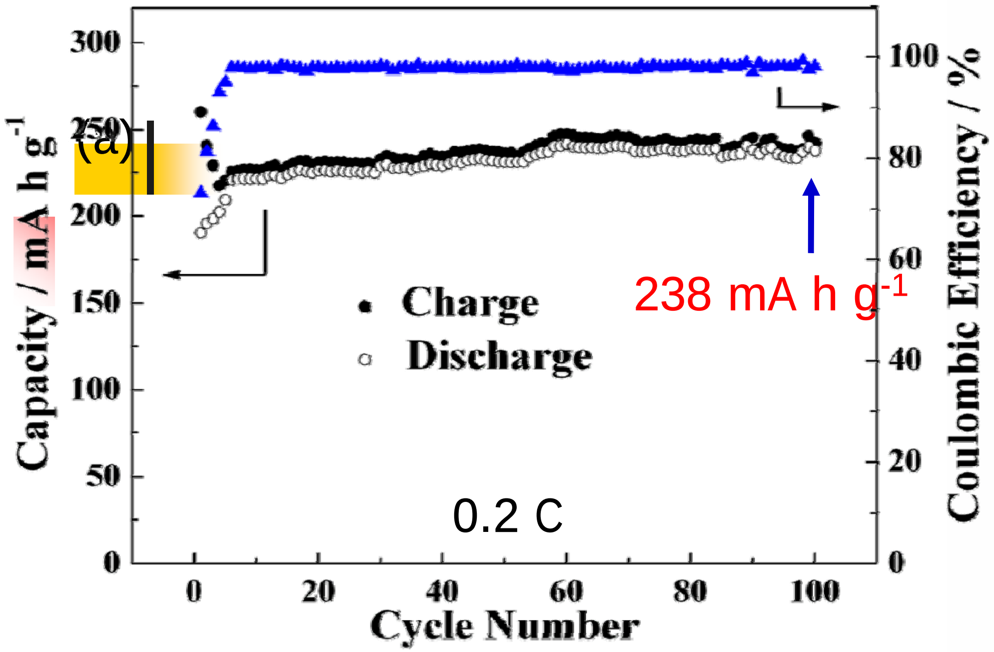


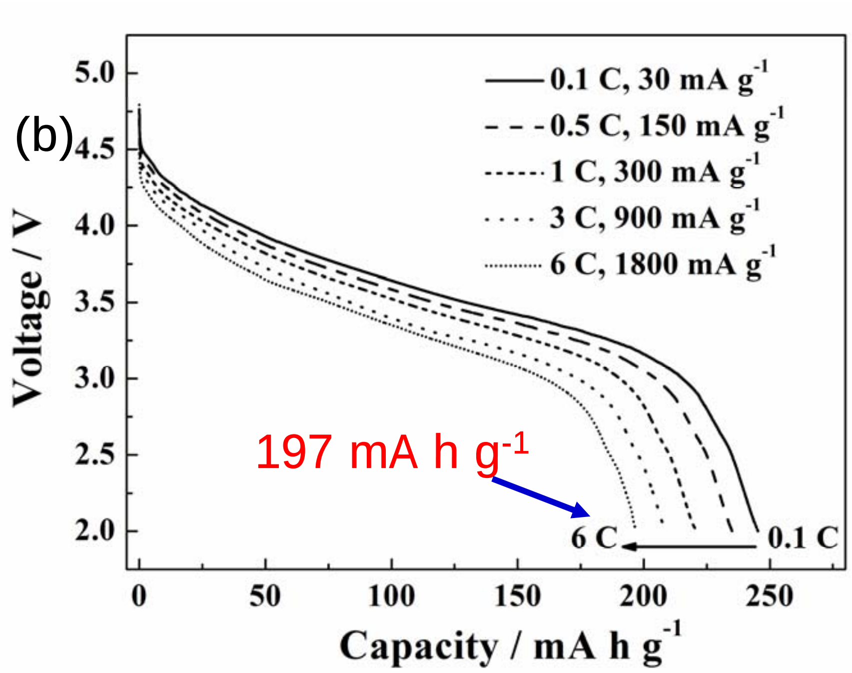


The proportion of the (010)- (and (100)-) nanoplates in HTN-LNMO is about 1/7. It signifies that the active surfaces would increase by about 50% in compared with CN-LNMO



TEM Characterization



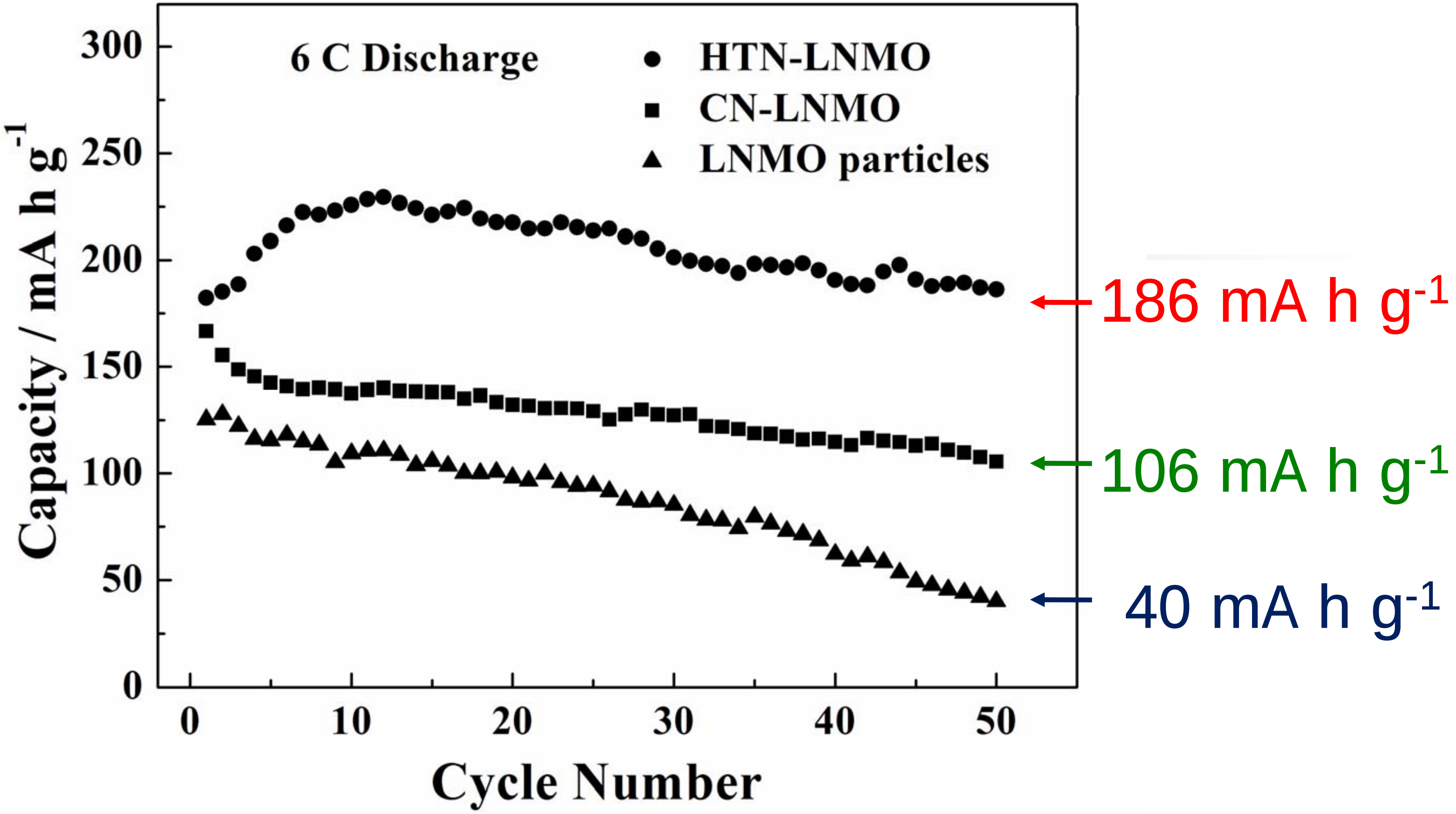


Cycle-ability and rate-capability of HTN-LNMO.

(a) Specific capacity vs. cycle number plots of electrodes prepared from HTN-LNMO. Test conditions: current density = 60 mA g^{-1} (about 0.2 C), voltage window = 2.0 - 4.8 V.

(b) Stabilized discharge voltage profiles of HTN-LNMO cycled at different rates: 6, 3, 1, 0.5, 0.1 C from bottom to top.

G.Z. Wei, S.G. Sun et al. Adv.Mater., 2010, 22: 4364-4367



Discharge capacity at a 6 C rate and cycleability of **HTN-LNMO** compared with **CN-LNMO** and **LNMO particles**.

G.Z. Wei, S.G. Sun et al. Adv.Mater., 2010, 22: 4364-4367

2. Lithium nickel cobalt manganese (LNCM) hexagonal nanobricks as cathode of lithium ion battery

- Shape-controlled $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ nanomaterials of high surface energy and high rate-capability

Layered Transition-metal Oxide

Advantages of LNCM:

- High theoretical capacity (275 mAh g^{-1})
- Zero phase change in the voltage range of 2.5-4.4 V
- Good thermal stability
- High safety

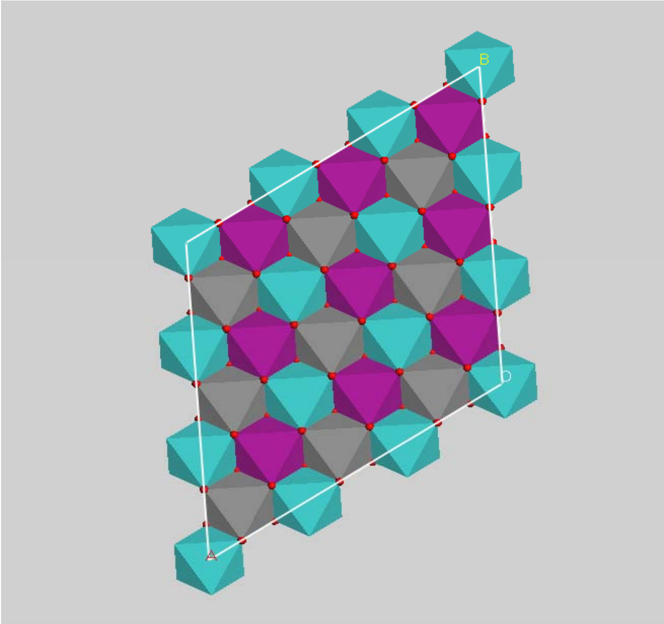
Some drawbacks of LNCM:

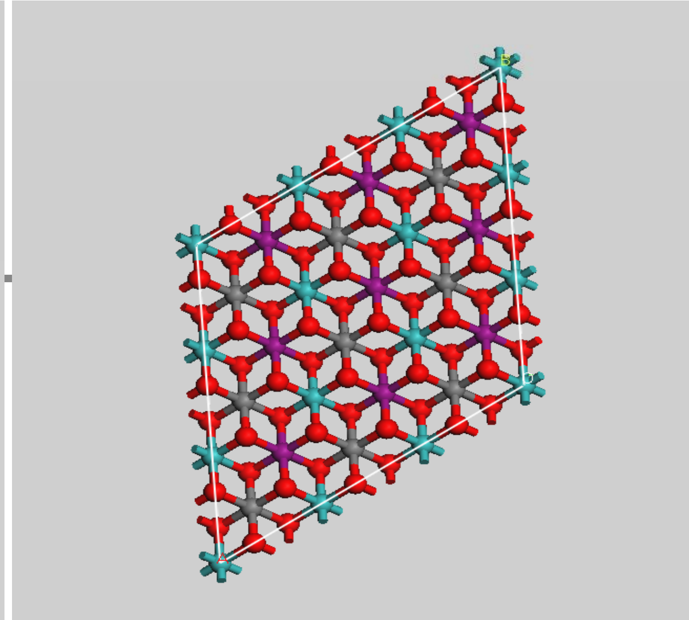
Rapidly fading capacity and poor rate-capability, which inhabit its further use in the electrical vehicle applications.

Focus of this work

Improve the electrochemical performances of the materials by tuning the shape of crystal to increase the proportion of active plane for Li^+ deintercalation/intercalation.

{001} surface of hexagonal nanobrick

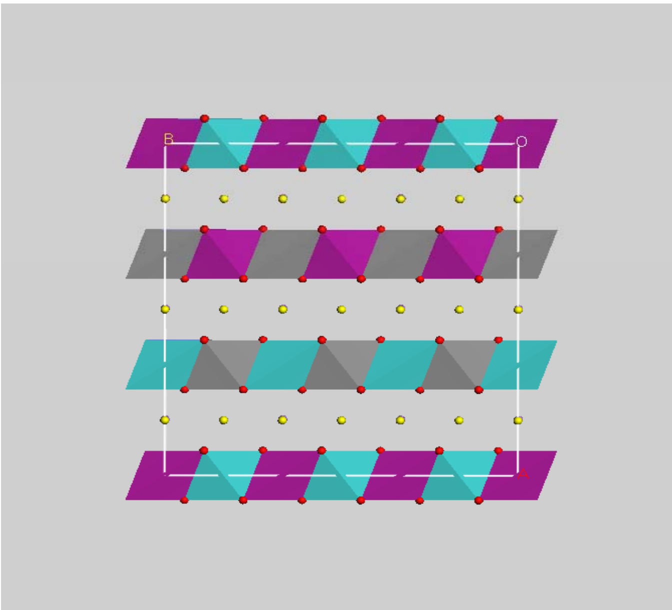


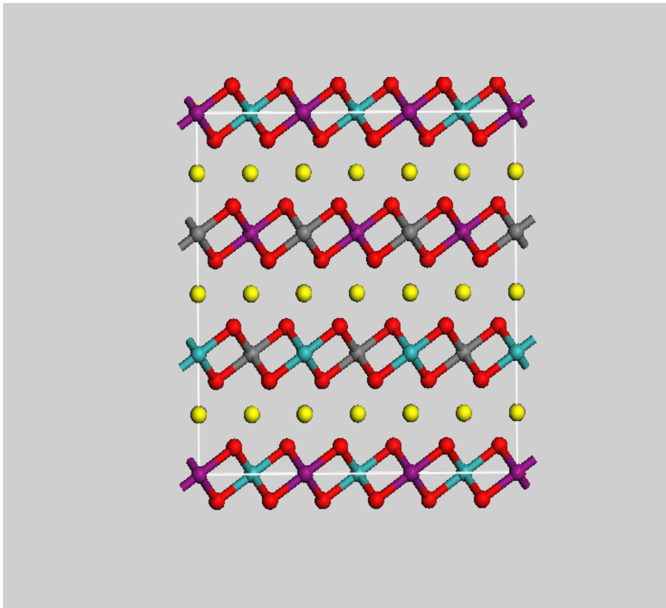


{001} surface takes on a closed-packed structure, which may hinder Li^+ transfer along [001] direction (c axies).

Viewed down c axis

{010} surface of hexagonal nanobrick, which is equivalent to other five lateral planes



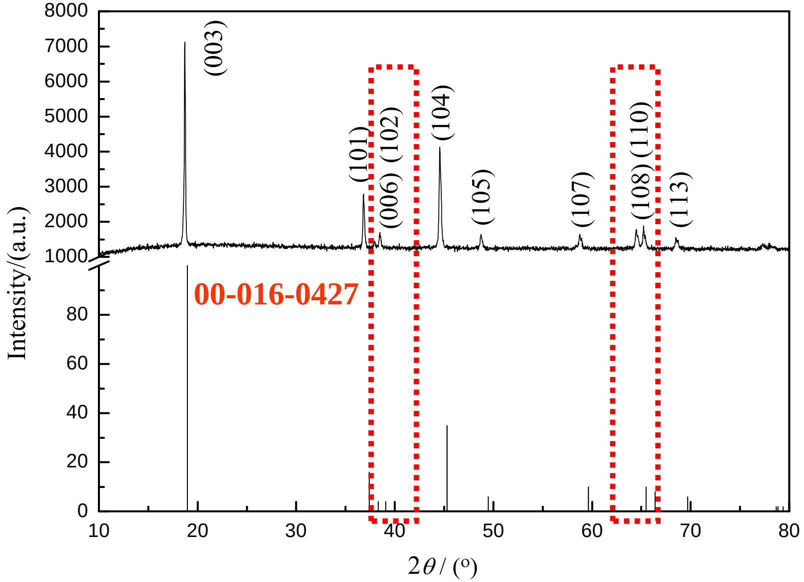


The channels are perpendicular to [001] direction with much space for Li^+ deintercalation /intercalation, so increase the thickness of nanobrick may enhance the active plane for Li^+ transfer.

Viewed down b axis

XRD analysis of LNCM Hexagonal nanobricks

Hexagonal α-$NaFeO_2$ structure
with R3m space group

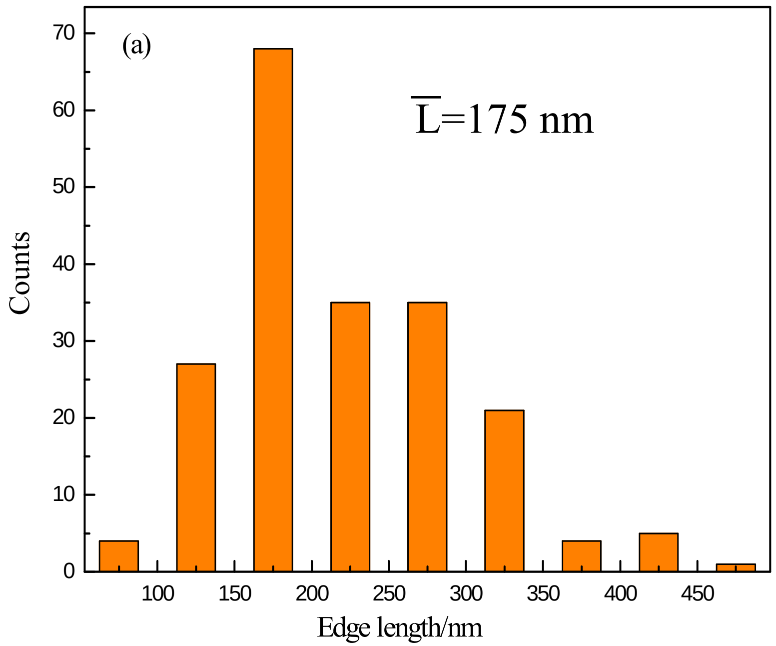


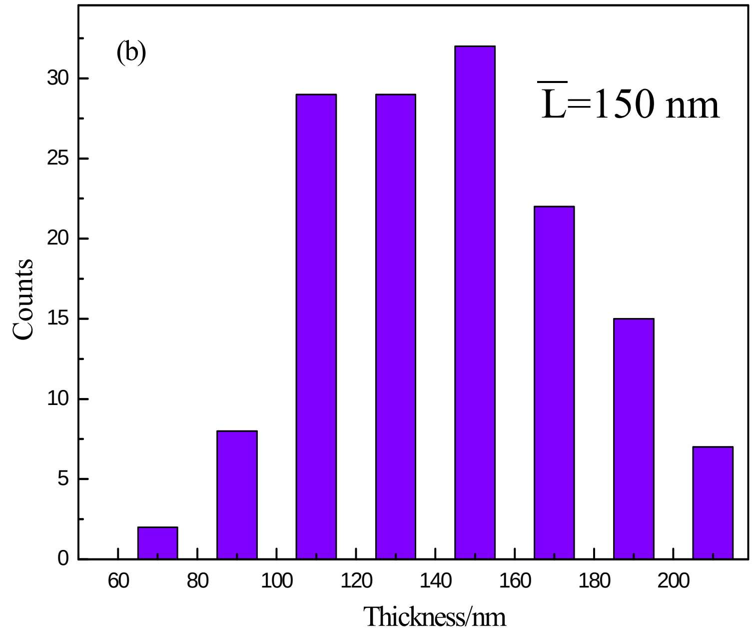
XRD pattern of LNCM hexagonal nanobricks

Sample	Lattice Parameters			I(003)/I(104)	R value	$\triangle\theta_1$	$\triangle\theta_2$
	a(A◦)	c(A◦)	c/a				
LNCM hexagonal nanobricks	2. 8589	14.2208	4.9742	2.06	0.365	0.5328	0.7233
Literature	2.8565	14.217	4.977	-	-	-	-

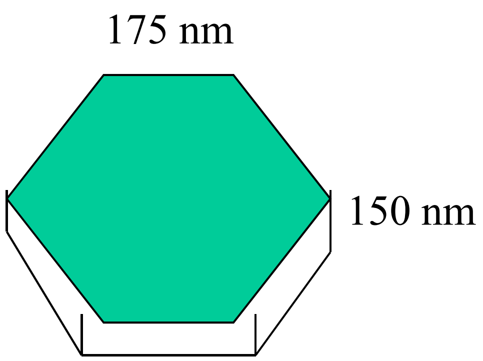
- ➢A clear split of (0 0 6)/(102) and (108)/(1 1 0) peaks ishows a well developed layered-structure.
- ➢I(003)/I(104) was larger han 1.2 indicates low cation mixing.

Edge length and thickness distribution of hexagonal nanobricks





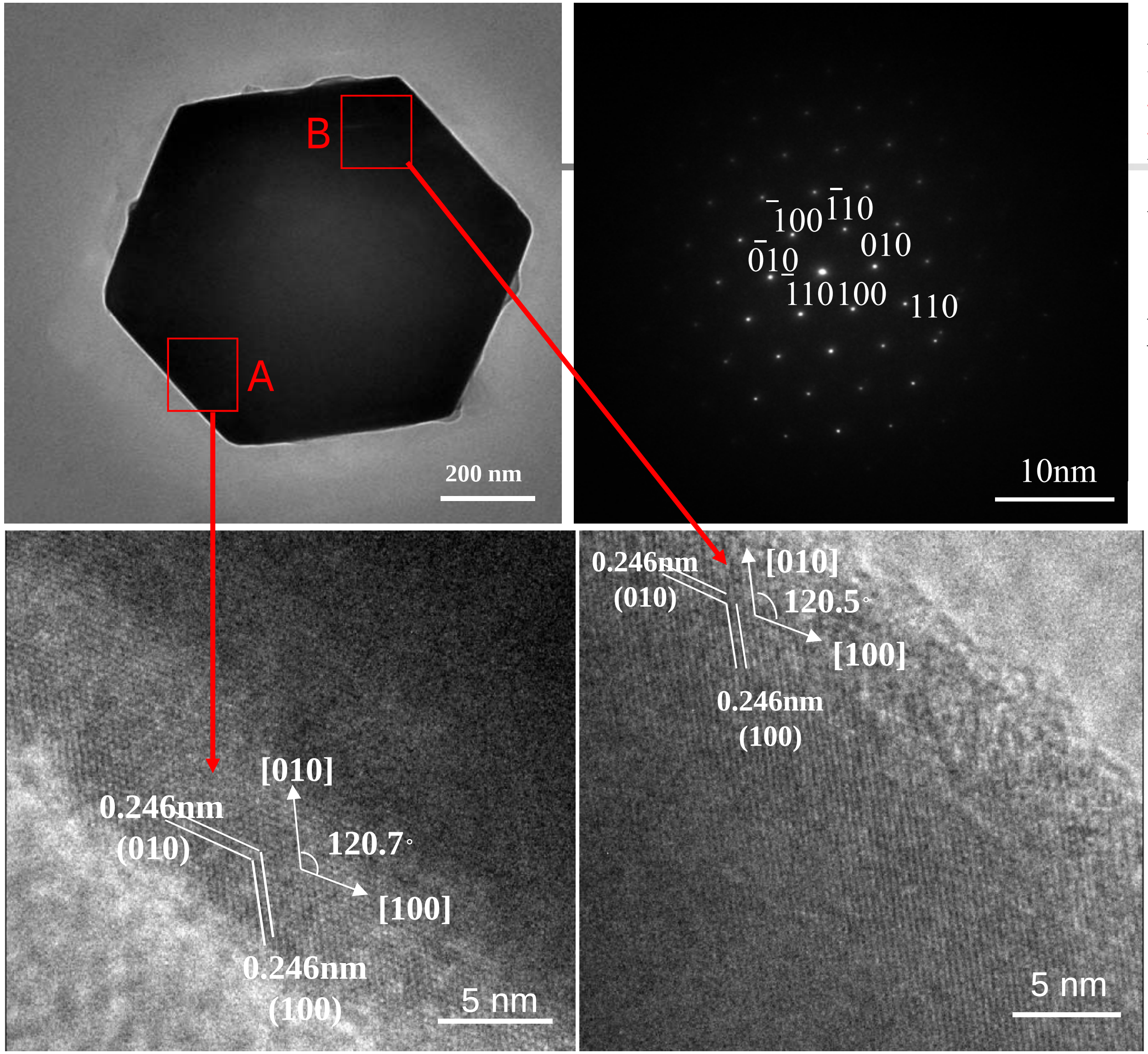
Edge length and thickness distribution of hexagonal nanobricks



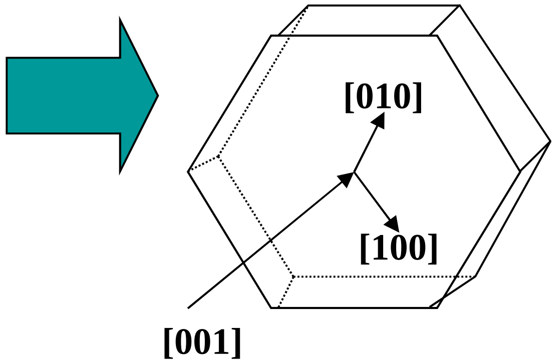
The model of the hexagonal nanobrick

The ratio of the lateral view to the total surface area of nanobrick is found to be approximately **57.9%** by calculating from the model.

Plane analysis of **the frontal view** of LNCM nanobricks



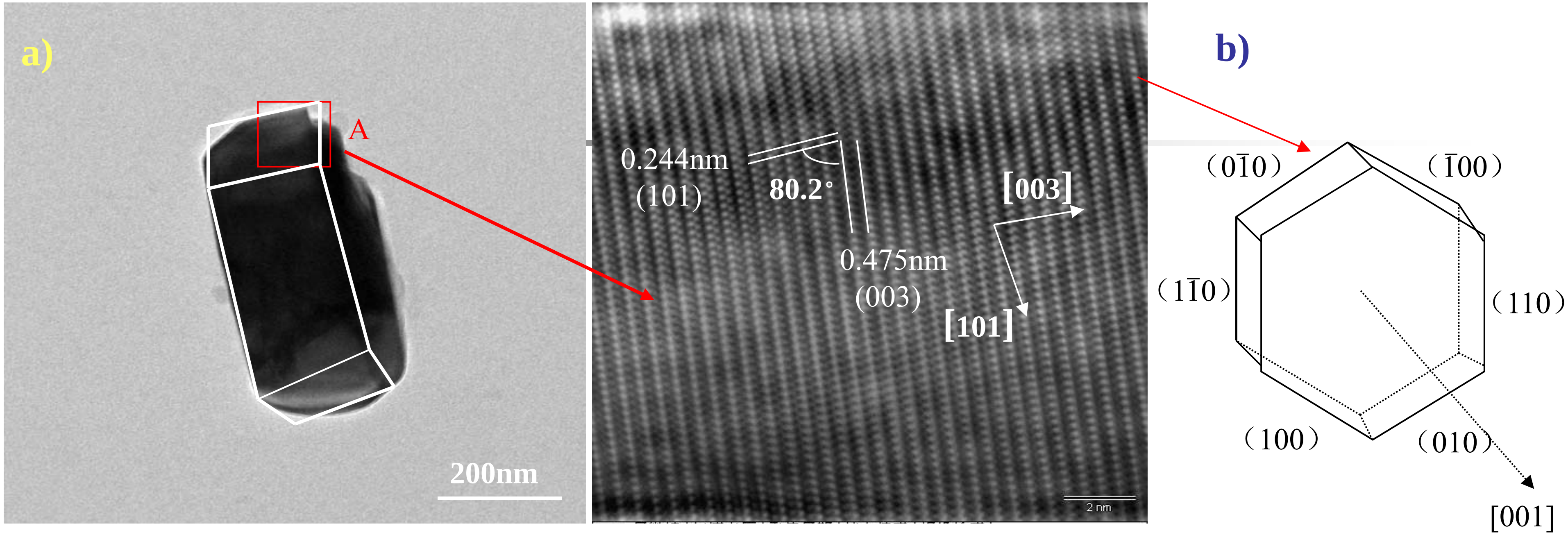
The frontal plane of LNCM hexagonal nanobricks is **(001) plane**, which is the plane normal to both the set of (100) planes with a crossing lattice space of 0.246 nm and the set of (010) planes with a lattice space of 0.246 nm.



Structure model of hexagonal nanobricks

HRTEM image and SAeD pattern of the frontal view of LNCM hexagonal nanobricks

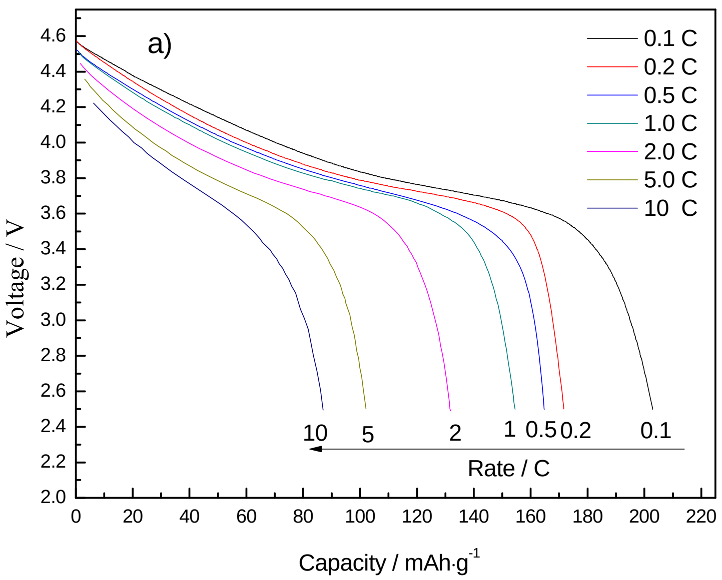
Plane analysis of **the lateral view** of LNCM nanobricks

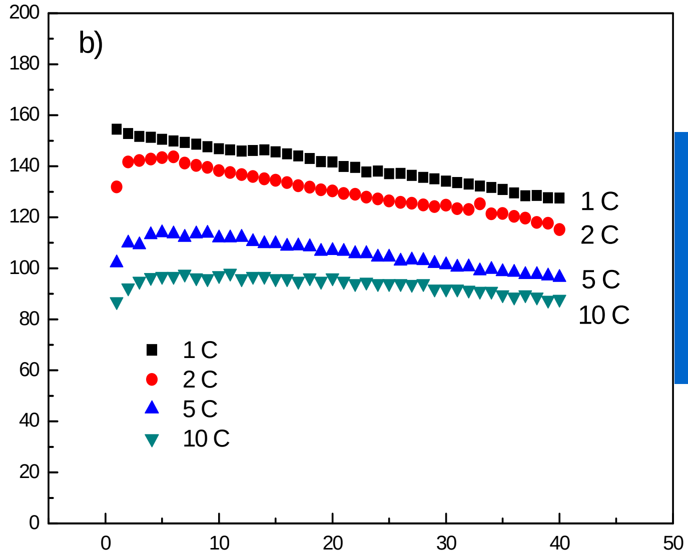


a) HRTEM image of the lateral view of LNCM hexagonal nanobricks ;b) Structure model of hexagonal nanodics

One lateral plane of LNCM hexagonal nanobricks is **(010) plane**, the remaining five planes are (110), (100), (010), (110), (100), which can be able to infer from the hexagonal structure. These lateral planes of LNCM nanobricks are signficant since they are normal to **the most facile pathway** for lithium ion conduction,and hence important for the reversible insertion/de-insertion of lithium ions.

Rate capacity of LNCM Hexagonal nanobricks





82.5%
87.3%
94.4%
101%

a) Rate capability of LNCM hexagonal nanobricks. b) discharge capacity retentions of LNCM hexagonal nanobricks at various rate measured in the voltage range of 2.5-4.6 V.

Rate	0.1C	0.2C	0.5C	1C	2C	5C	10C
Discharge capacity ($mAh\ g^{-1}$)	202.9	171.7	164.8	154.5	131.9	102.1	87

At 1C and 5C rates, the electrodes were able to deliver 154.5 mAh/g and 102.1 mAh/g, respectively, corresponding to **89.9%** and **59.5%** of that of 0.2C,this indicates the promising rate capability of the material. Moreover, iIt has better cycle stability at high rate.

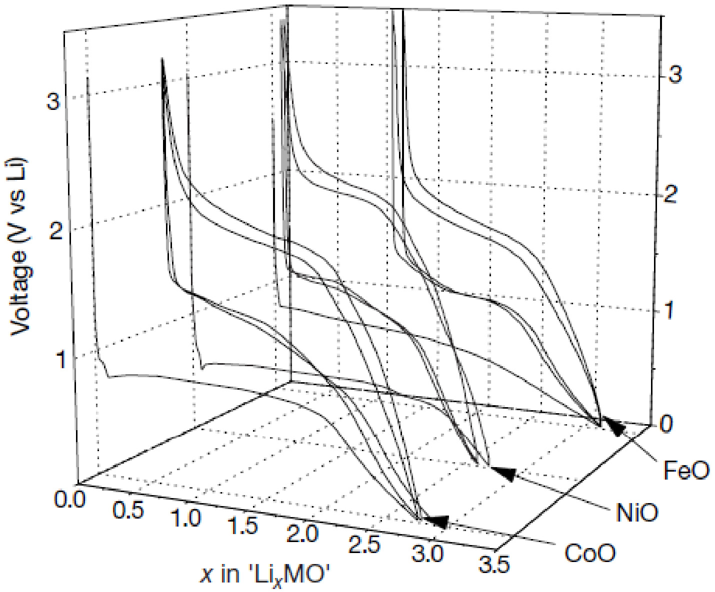
Summery

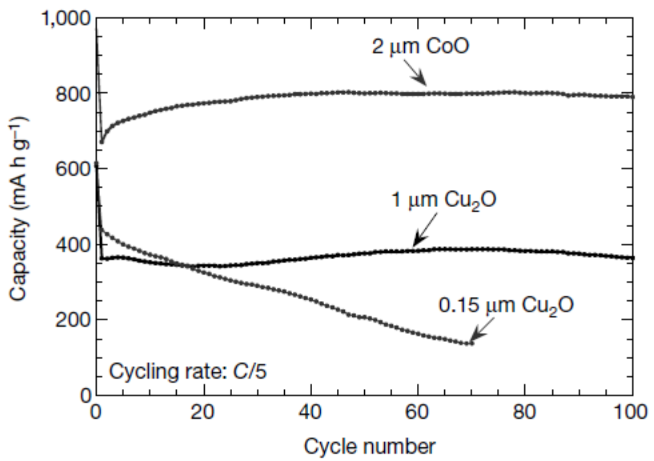
- The prepared LNCM material takes on a hexagonal nanobricks appearance ,with {001} as frontal planes and {100}/{010}as lateral planes .
- The lateral planes of LNCM nanobricks perpendicular to the {001} plane are active planes for Li^+ deintercalation/intercalation.
- Increasing the crystal size along [001] direction is an efficient way to enhance the electrochemical performance of the material.

3. Co_3O_4 octahedra and their high performances as anode of lithium ion battery

- Shape-control of Co_3O_4 nanomaterials
- The surface structure effects
- The size effects

The transition metal oxides and their conversion reaction





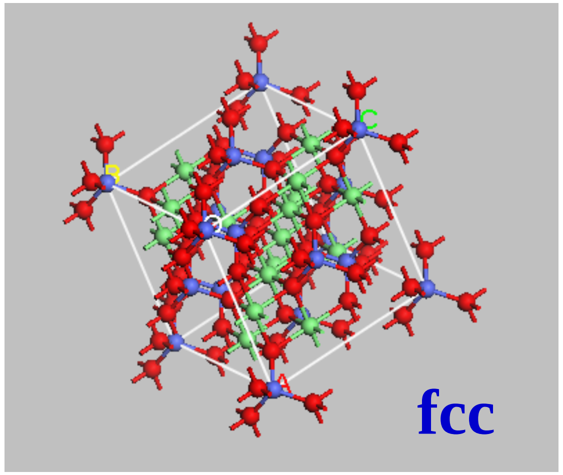
Based on a reaction mechanism of **conversion reaction** rather than intercalation/de-intercalation, transition metal oxides（Fe_2O_3, Fe_3O_4, Co_3O_4, CoO, NiO……）could deliver much higher capacity than commercial graphite

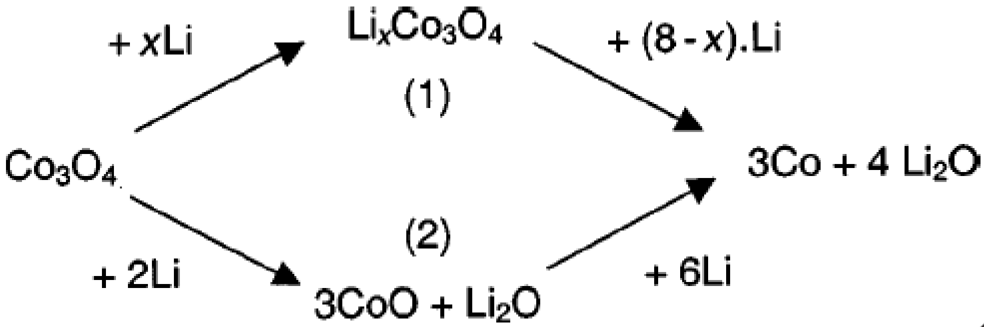
$$Li + MO \leftrightarrow M + Li_2O$$

particle size has a great influence on the electrochemical performance of the electrodes

Tarascon, J. M., *Nature* 407(6803): 496-499.

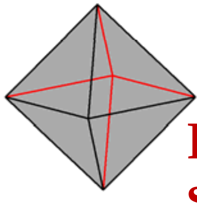
The Co_3O_4 material



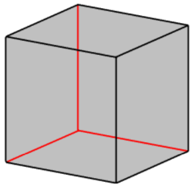


D. Larcher et al. JES, 149 (3) A234-A241(2002)

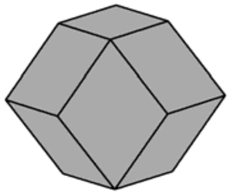
Octahedron {111}



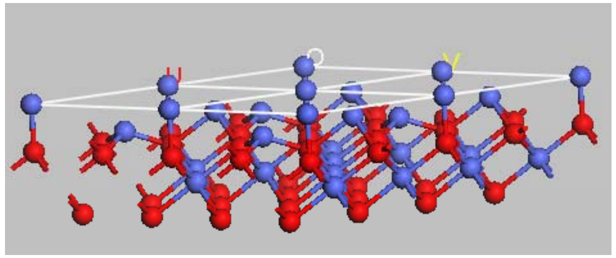
Polar surface

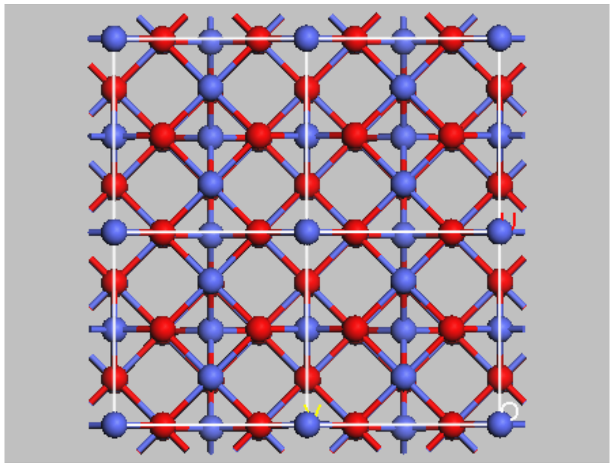


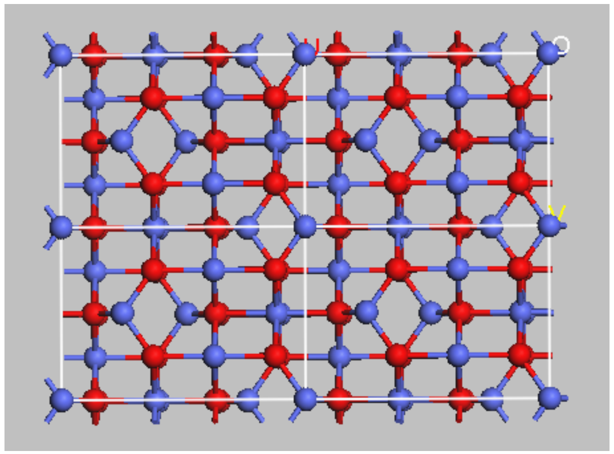
Cube {100}

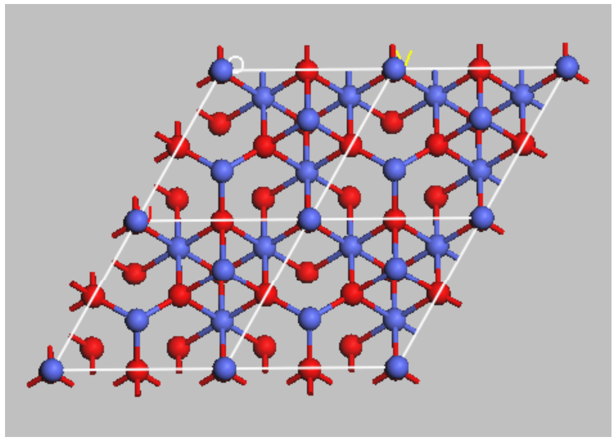


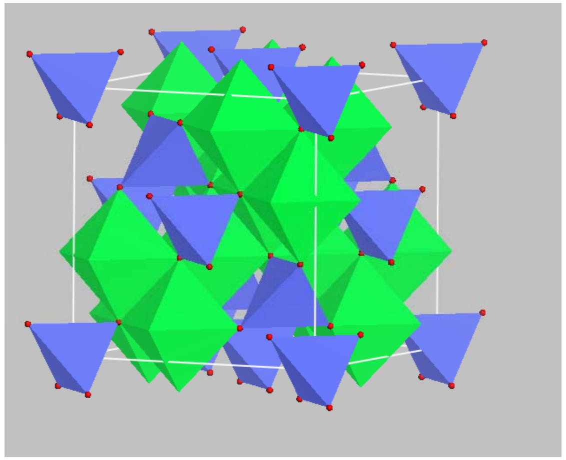
Dodeca-hedron {110}



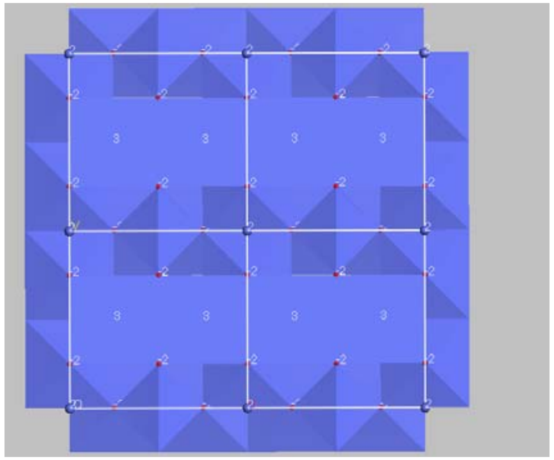




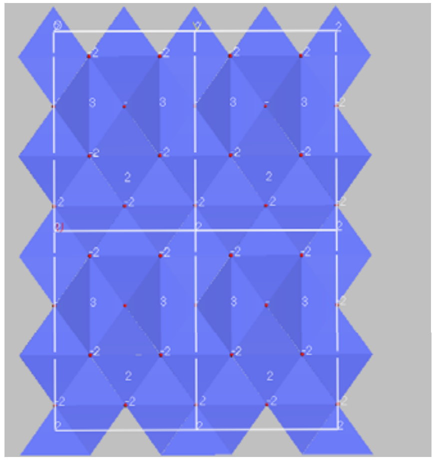




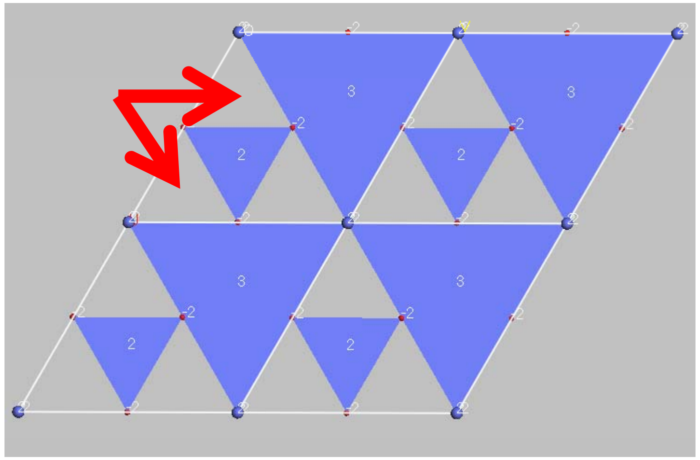
polyhedron model ,
the blue : cobalt (Ⅱ)
The green : cobalt (Ⅲ)



(100) plane of Co_3O_4

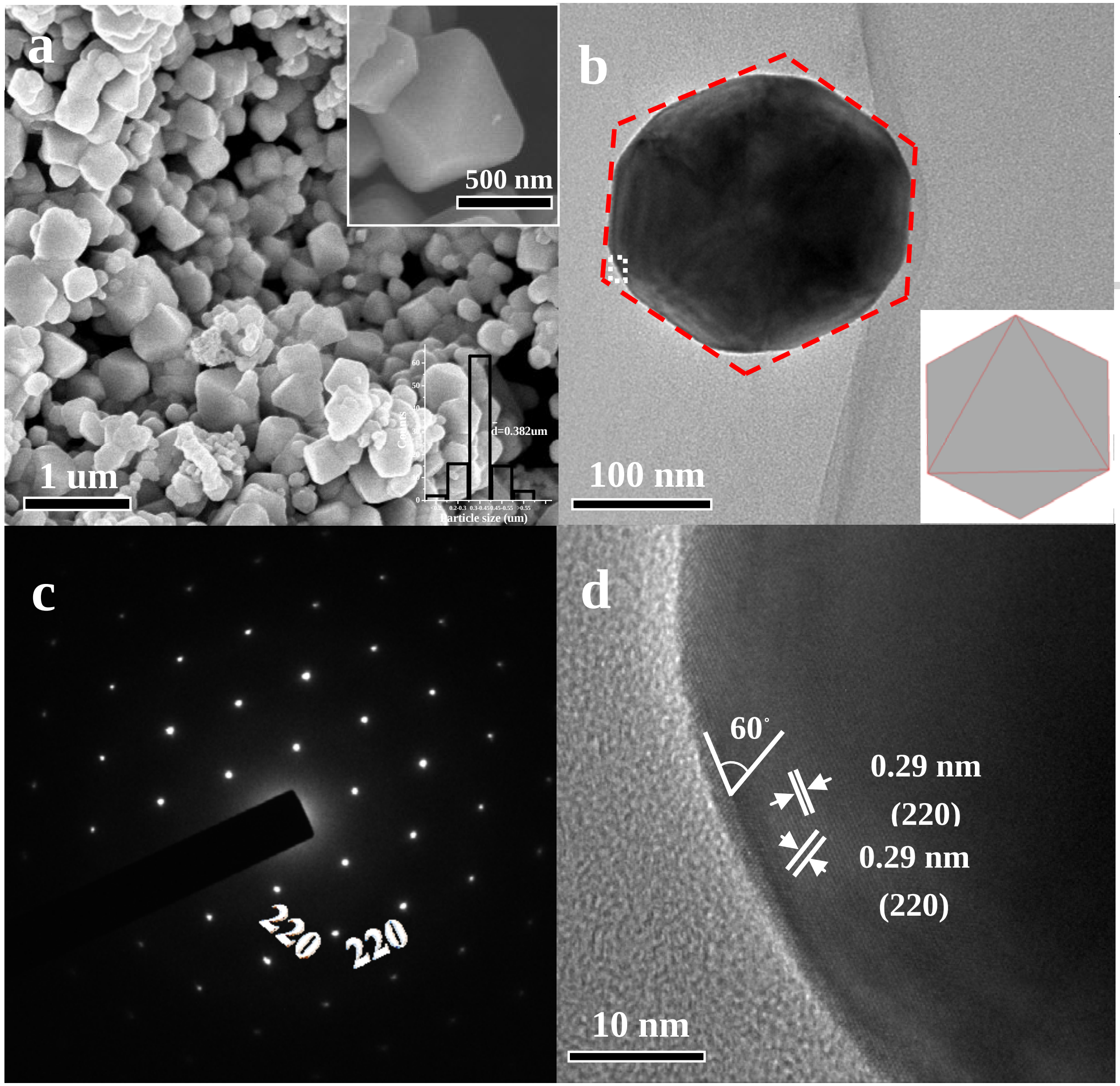


(110) plane of Co_3O_4.



(111) plane of Co_3O_4.

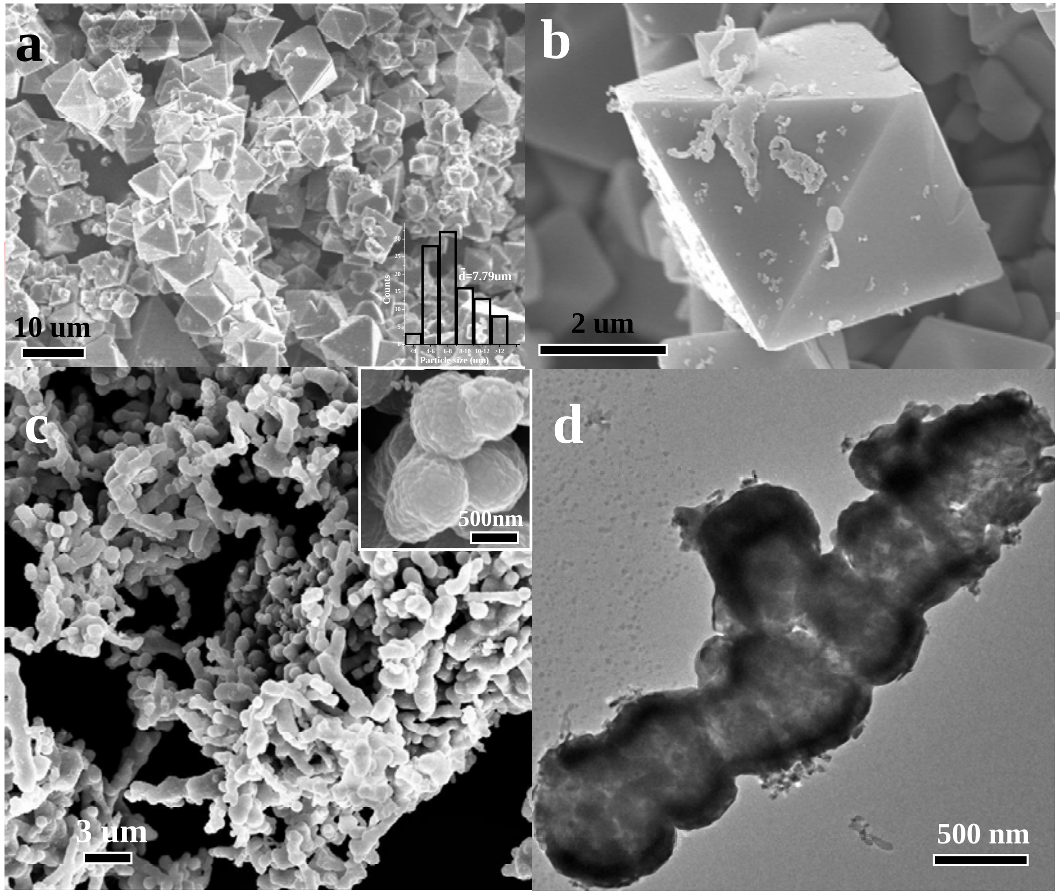
Open degree of surface structure	**(111) > (110) > (100)**



1. Nanosized octahedra Co_3O_4 was obtained with a particle size of 382 nm (**N-Co_3O_4**)

The individual N-Co_3O_4 particle is single crystalline

(a) SEM image of N-Co_3O_4, a magnified image (inset of Fig. 1a) and a size histogram of N-Co_3O_4 (100 particles) (inset of Fig. 1a). (b) TEM image of an individual particle of N-Co_3O_4 and a model profile of Co_3O_4 octahedra viewing from [111] direction. (e) The SAED pattern taken from the region marked by the white frame in Fig. 1b. (f) A HRTEM image taken from the region marked by the white frame in Fig. 1b.

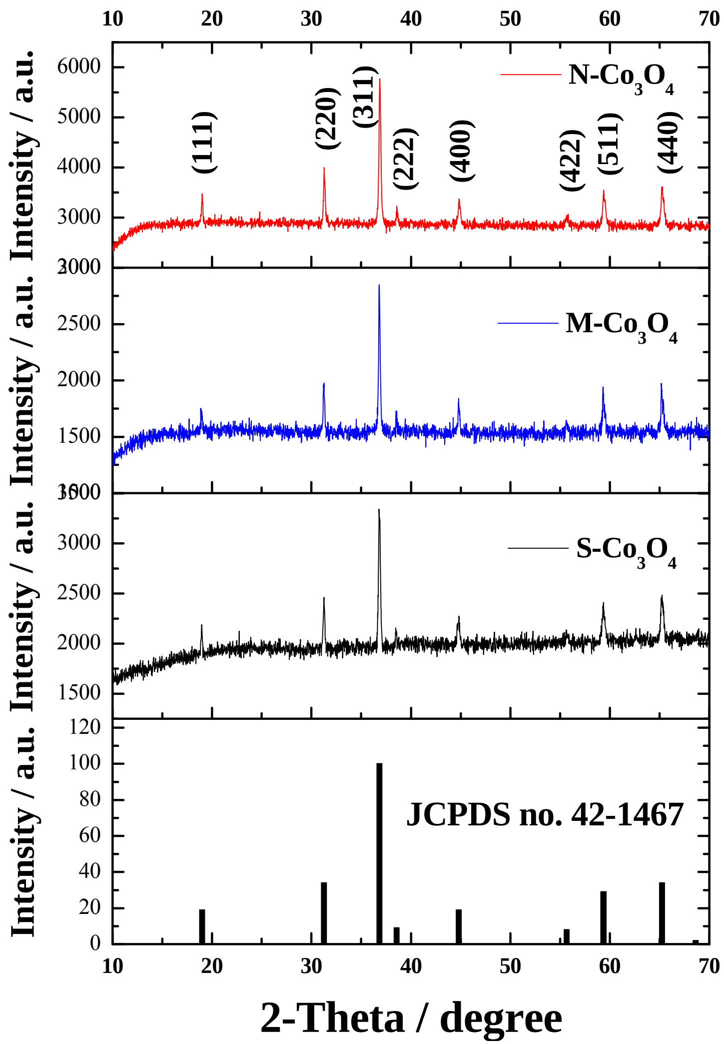


2. Microsized octahedra Co_3O_4 was obtained with a particle size of 7.79 um (**M-Co_3O_4**)

3. Spherical Co_3O_4 of average particle size of 500 nm (**S-Co_3O_4**)

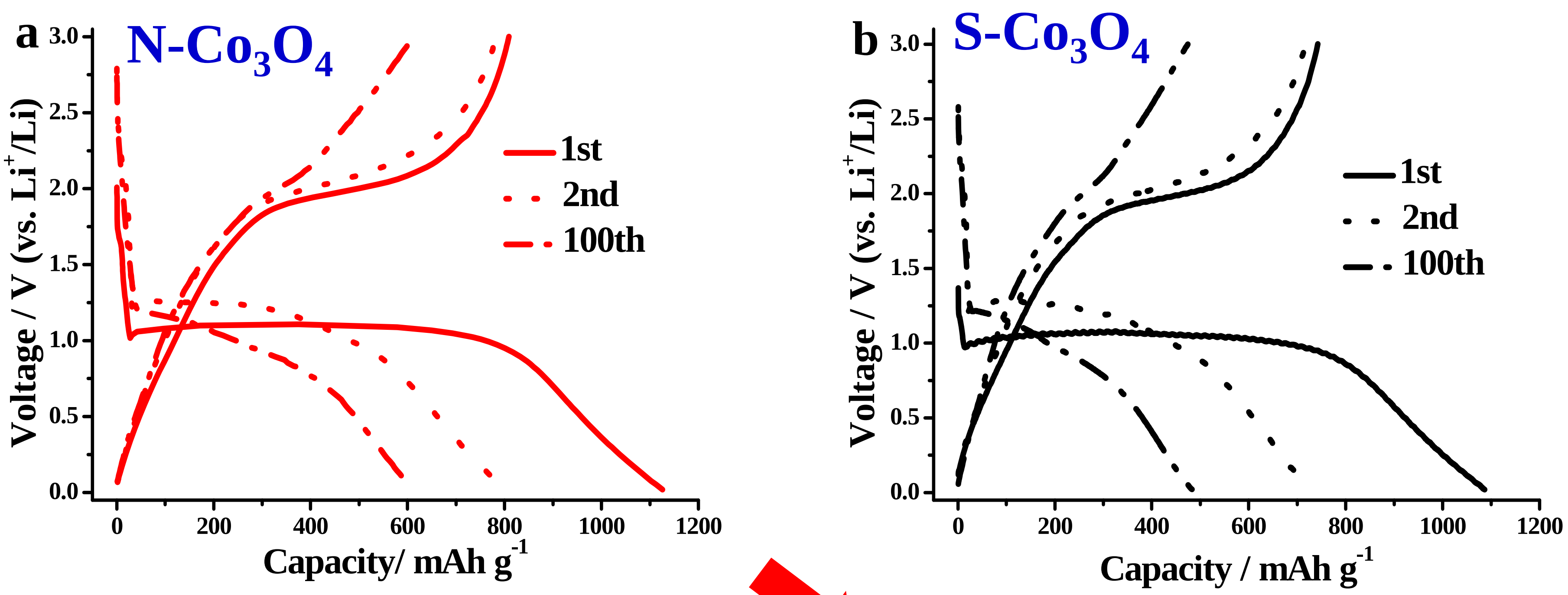
(a) SEM image of M-Co_3O_4 and a size histogram of M-Co_3O_4 (100 particles) (inset of Fig. 2a). (b) SEM image of an individual particle of M-Co_3O_4. (c) SEM image of S-Co_3O_4 and a magnified image (inset of Fig. 2c). (d) TEM image of S-Co_3O_4.

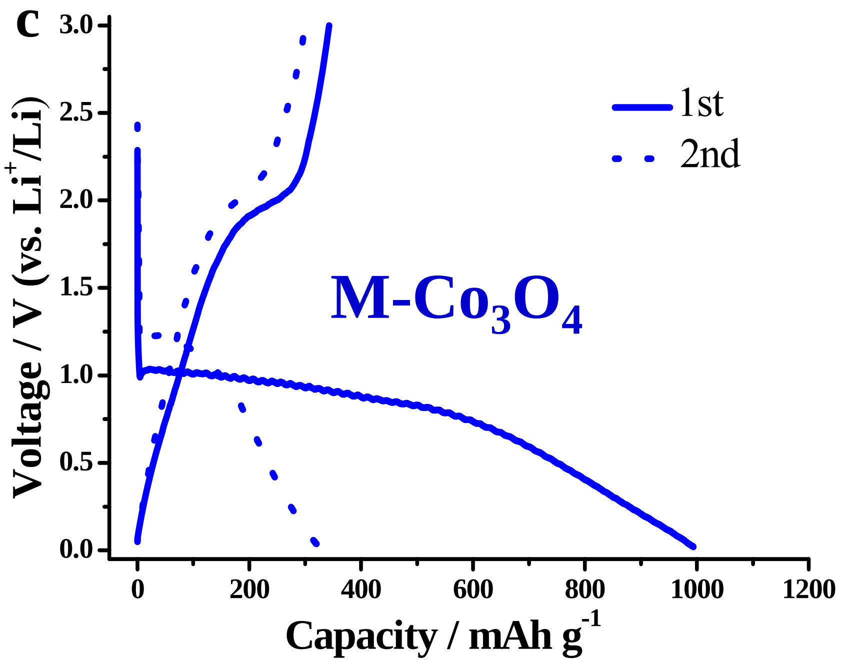
XRD characterization



All of the XRD patterns of three samples coincide with standard XRD pattern of Co_3O_4 (JCPDS no. 42-1467)

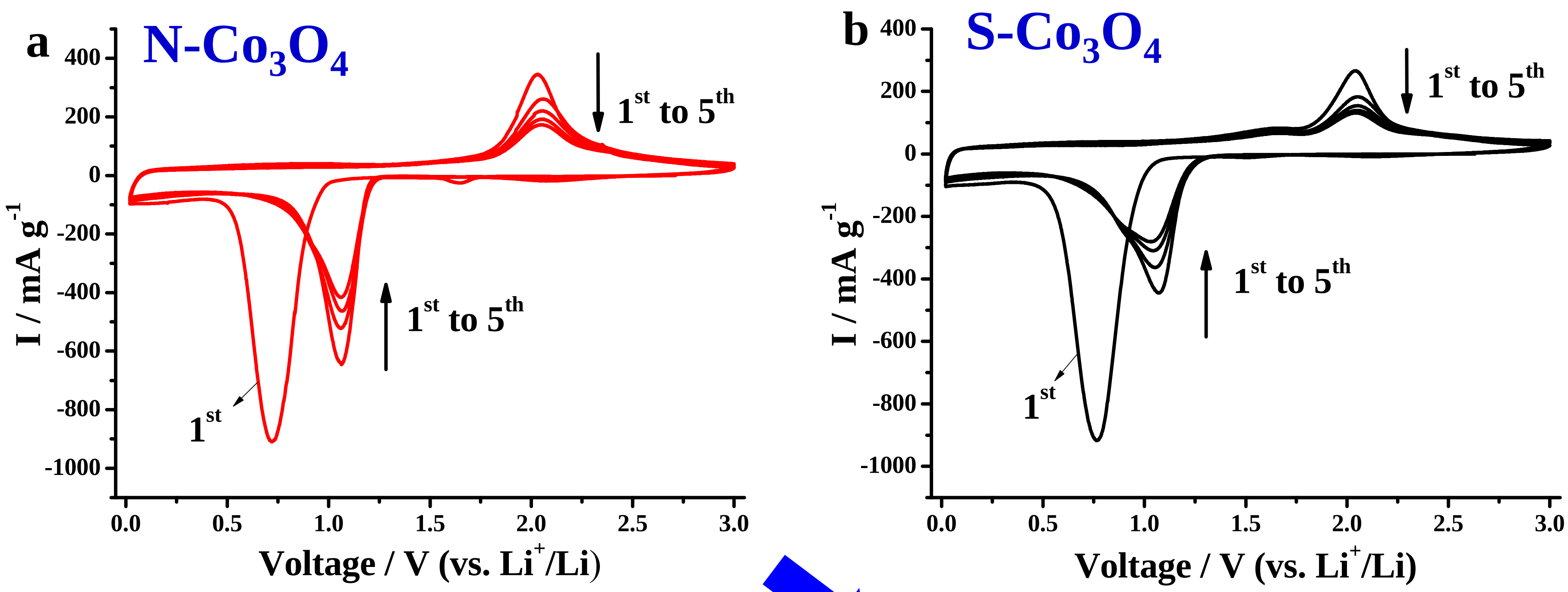
X-ray diffraction (XRD) patterns of N-Co_3O_4 (red line), M-Co_3O_4 (blue line), S-Co_3O_4 (black line) and the standard XRD pattern of Co_3O_4 (JCPDS no. 42-1467).

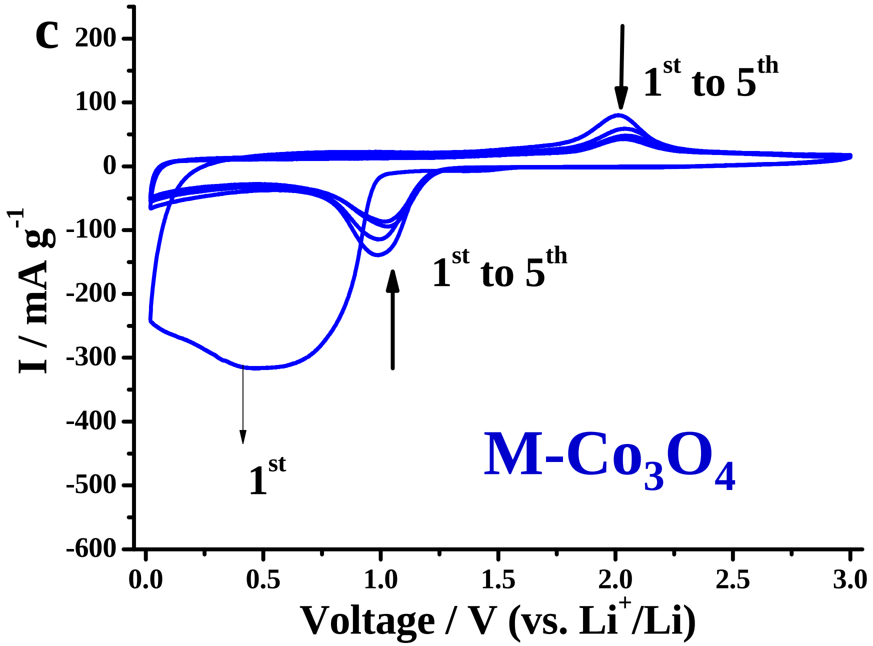




With increasing particle size of the electrodes, the polarization was also increased.

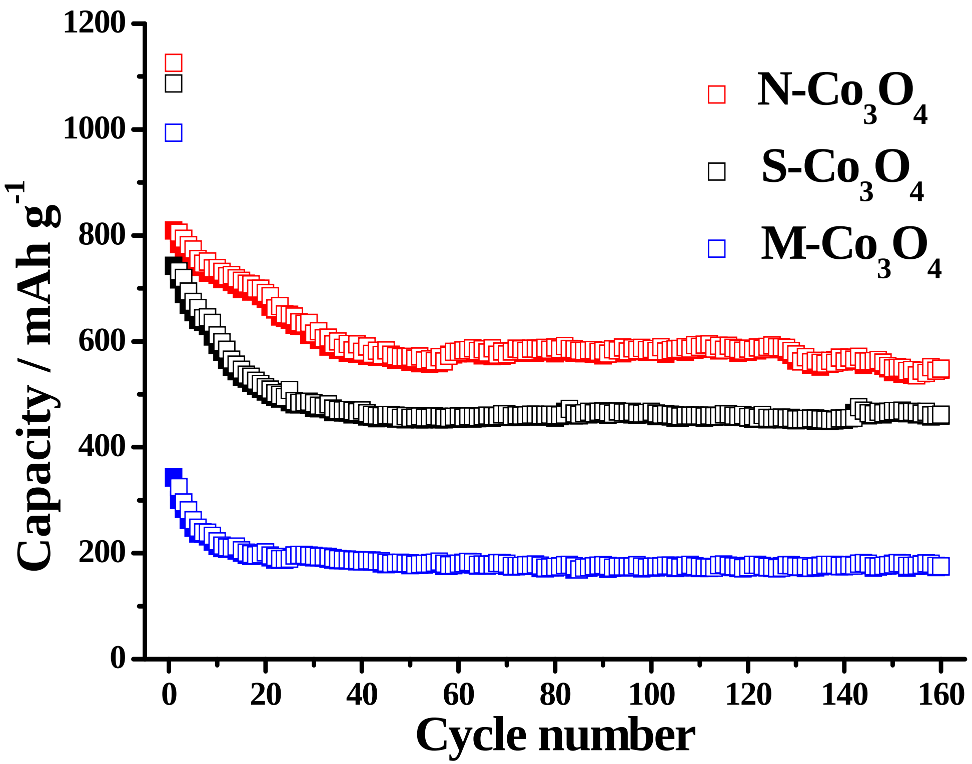
Typical charge-discharge curves at the current density of 100 mA g^{-1}





The results obtained from CV is in agreement with the charge-discharge profiles

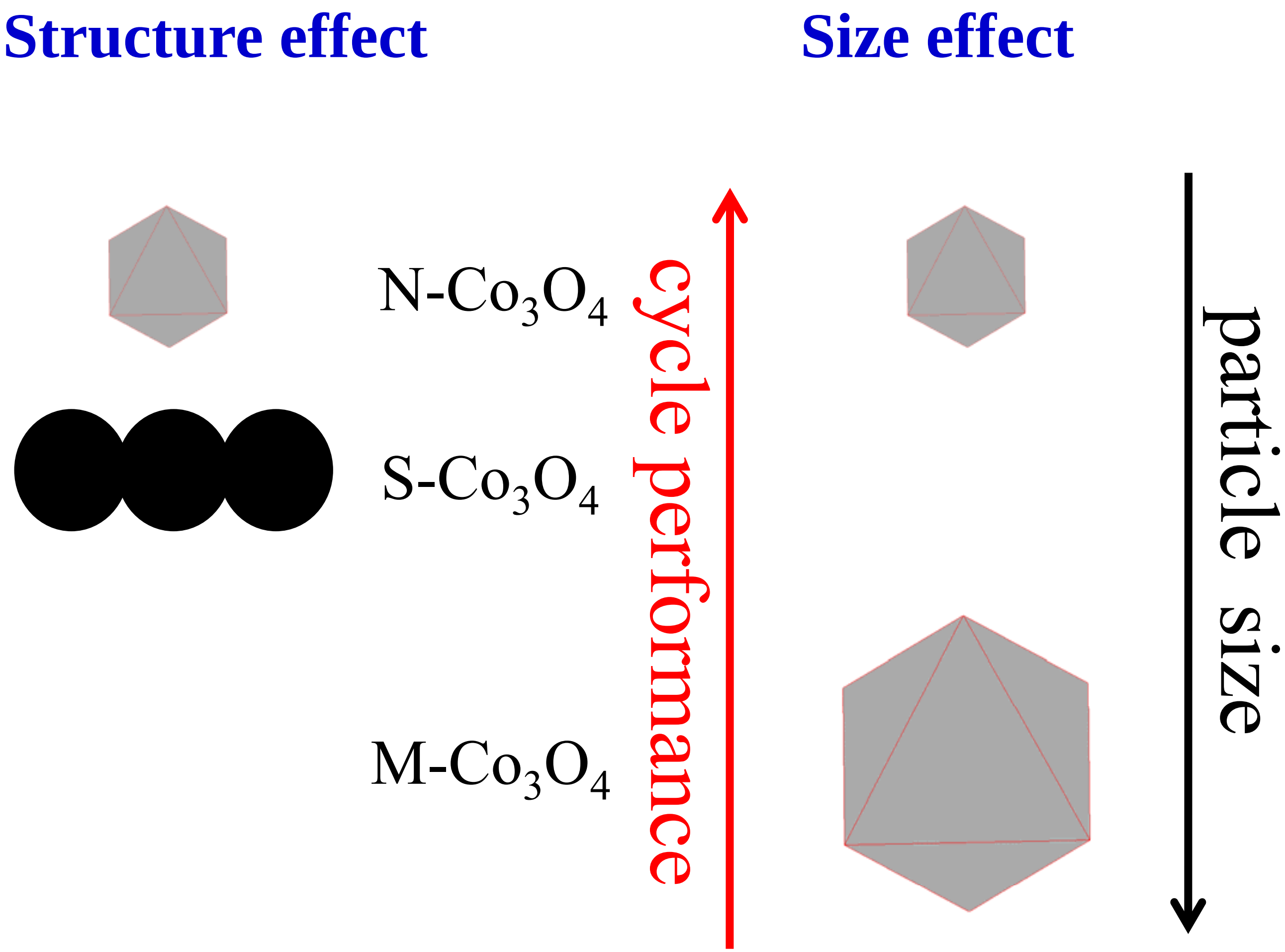
Cycle voltammograms at a scan rate of 0.1 mV s^{-1}.



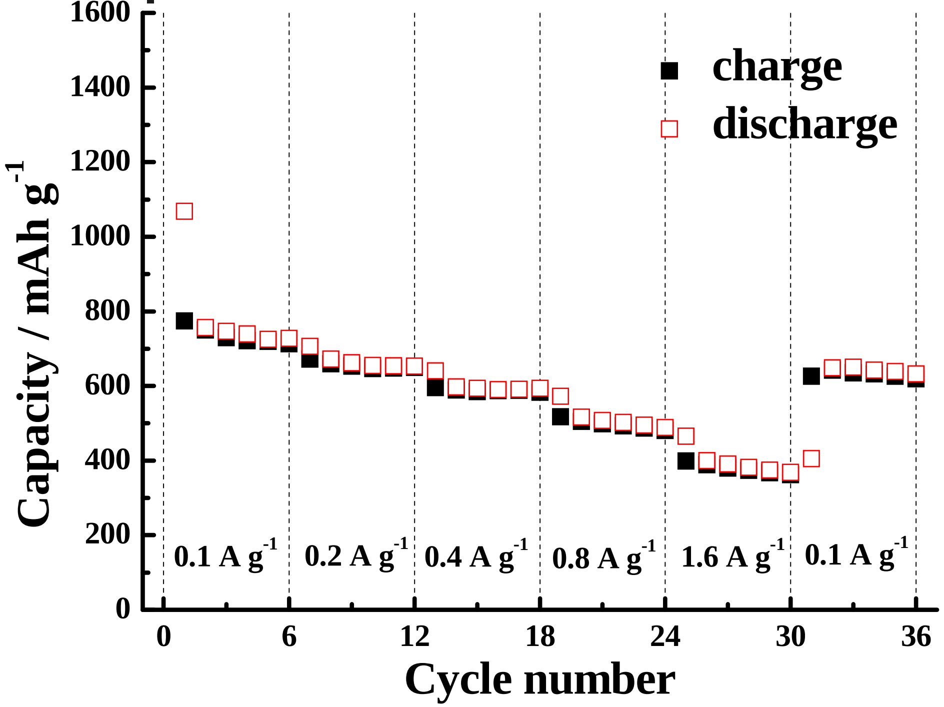
	$N\text{-}Co_3O_4$	$S\text{-}Co_3O_4$	$M\text{-}Co_3O_4$
1st discharge capacity (mAh g^{-1})	1125.6	1086.9	993.8
1st coulombic efficiency (%)	71.9	68.3	34.5
160th discharge capacity (mAh g^{-1})	548.5	459.6	175

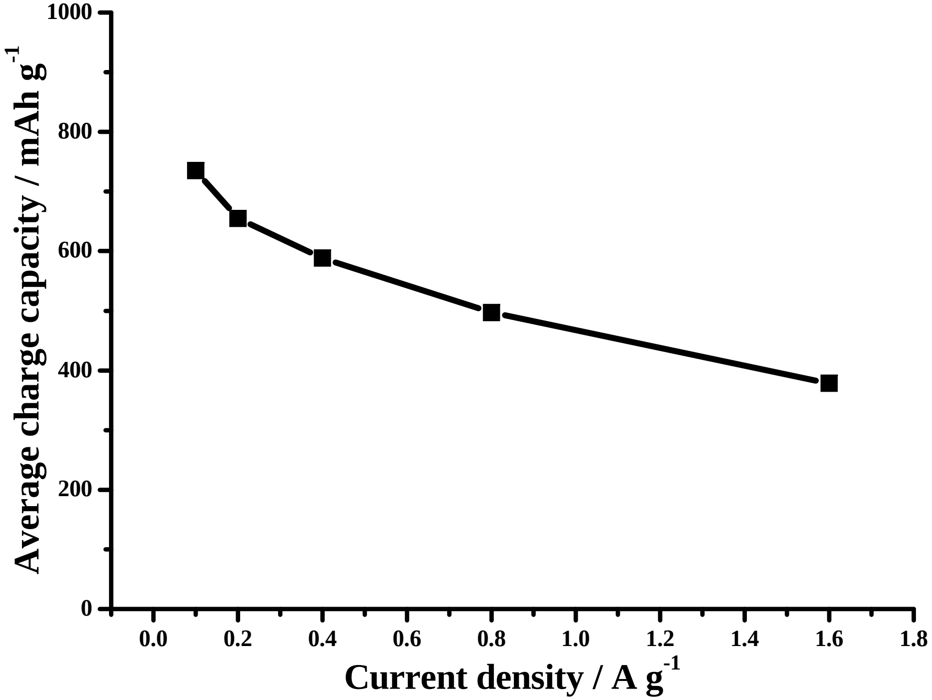
Cycle performance: $N\text{-}Co_3O_4 > S\text{-}Co_3O_4 > M\text{-}Co_3O_4$

Cycle performances of $N\text{-}Co_3O_4$, $S\text{-}Co_3O_4$ and $M\text{-}Co_3O_4$ electrodes at the constant current density of 100 mA g^{-1}. The solid and hollow symbols represent charge and discharge capacities, respectively.


Structure effect
Size effect
N-Co_3O_4
S-Co_3O_4
M-Co_3O_4
cycle performance
particle size

Rate capability of N-Co_3O_4





Rate capability of N-Co_3O_4 electrode. The current density was increased successively from 0.1 A g $^{-1}$ to 0.2 A g $^{-1}$, 0.4 A g $^{-1}$, 0.8 A g $^{-1}$ and 1.6 A g $^{-1}$. The solid and hollow symbols represent charge and discharge capacities, respectively.

3. Conclusions

- The open surface structure of materials is a key issue determining the property especially the rate-capability.
- The open surface structure corresponds to high surface energy, which leads to a big challenge in synthesis, thus shape-controlled methods need to be developed.
- The LNMO, NCM and Co_3O_4 nanomaterials with open surface structure reported in this lecture demonstrate the efficient way to further improve significantly the electrochemical performances of nanomaterials electrodes

Thank you for your attention !