Sustainable Nanostructured Materials for Energy Storage

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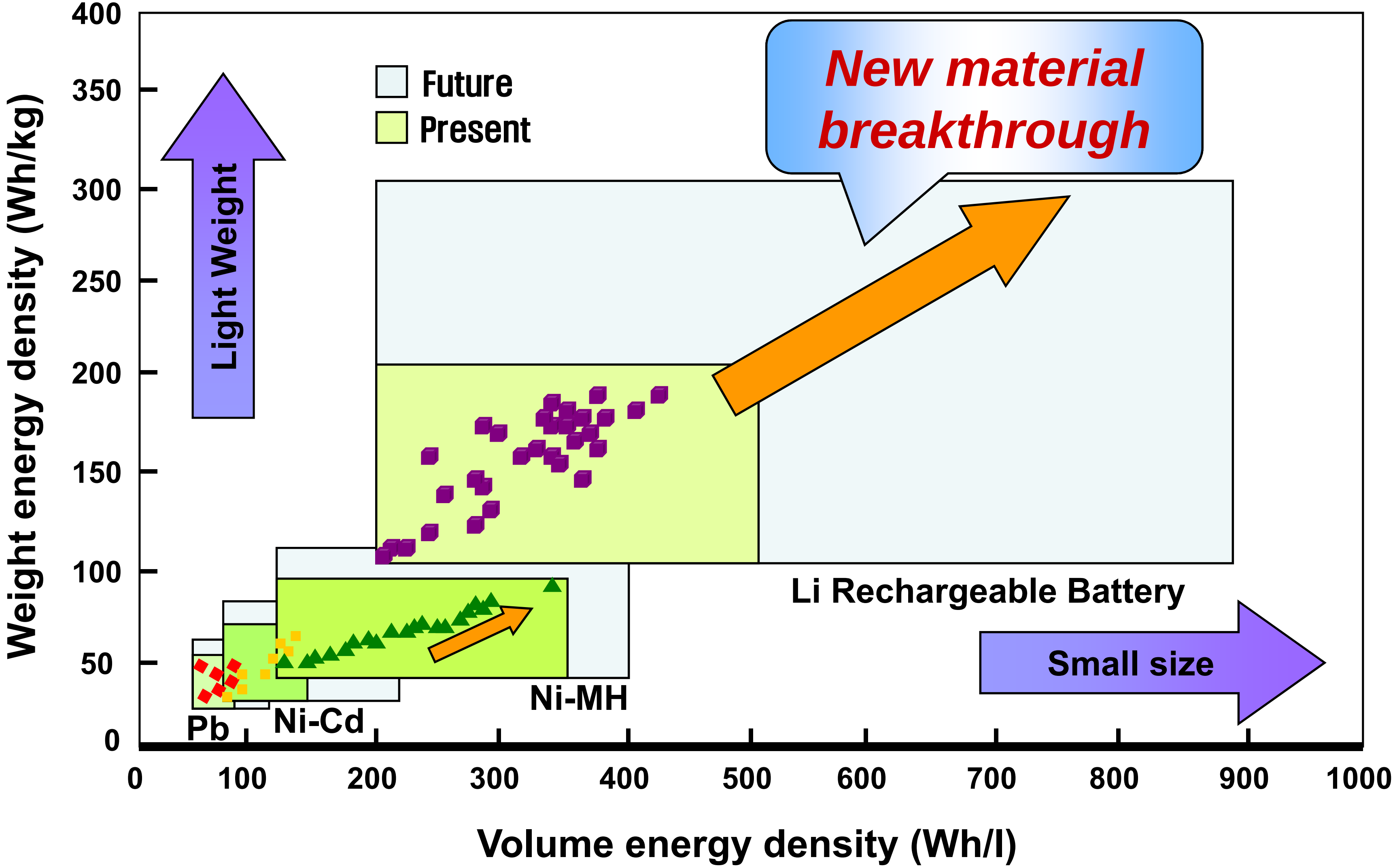
UNIST

Issues

- Capacity (Energy density)
- Flexibility
- Fast Charging/Discharging

R & D Target



Future
Present
New material breakthrough
Light Weight
Small size
Li Rechargeable Battery
Ni-MH
Ni-Cd
Pb
Weight energy density (Wh/kg)
0
50
100
150
200
250
300
350
400
Volume energy density (Wh/l)
0
100
200
300
400
500
600
700
800
900
1000

Contents

Introduction

Application area

1. Mobile Device

♣High Capacity
- Global Communication System
- 3G/4G

♣Good cycle life
- Cellular Phone
- Notebook

♣High Safety

♣Low Cost

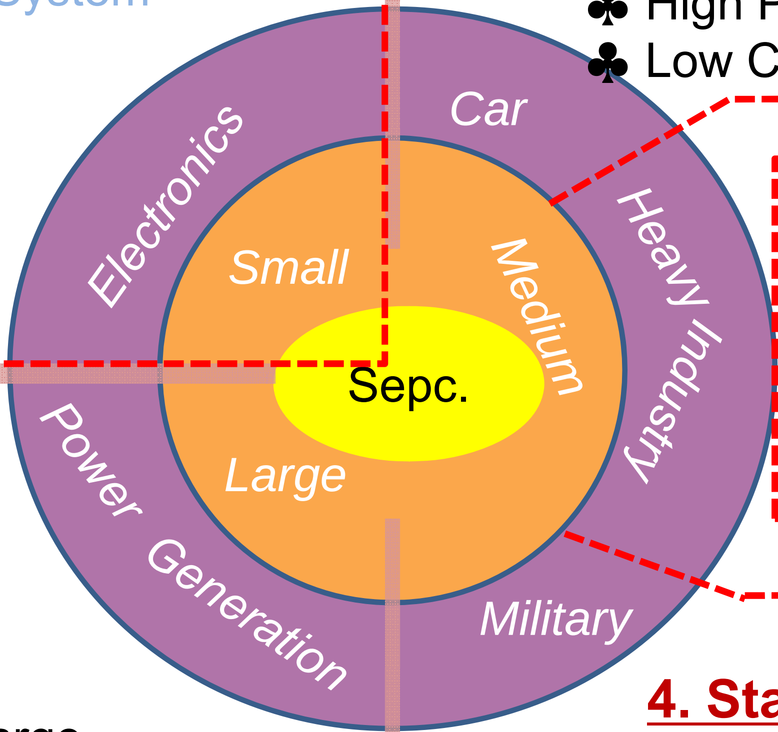
2. EV or HEV

♣ High Safety

♣ Wide temperature range

♣ High Power

♣ Low Cost



3. Power Tool

♣ High Power

♣ Fast Charging/Discharging

♣ Low Cost

4. Stationary Battery

♣ High Power

♣ Maintenance Free

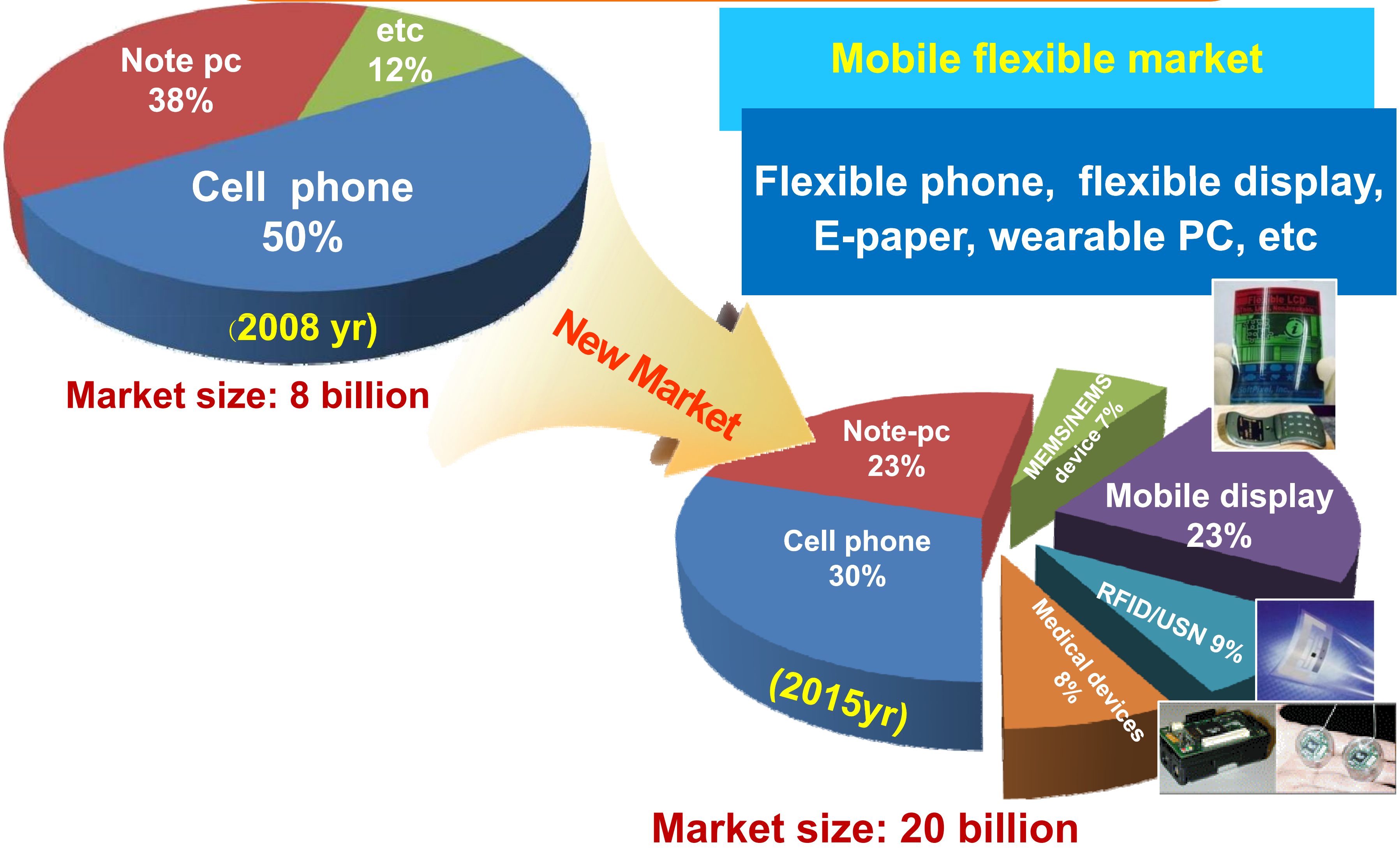
5.Energy Storage

♣ Maintenance Free (excellent cycle life)

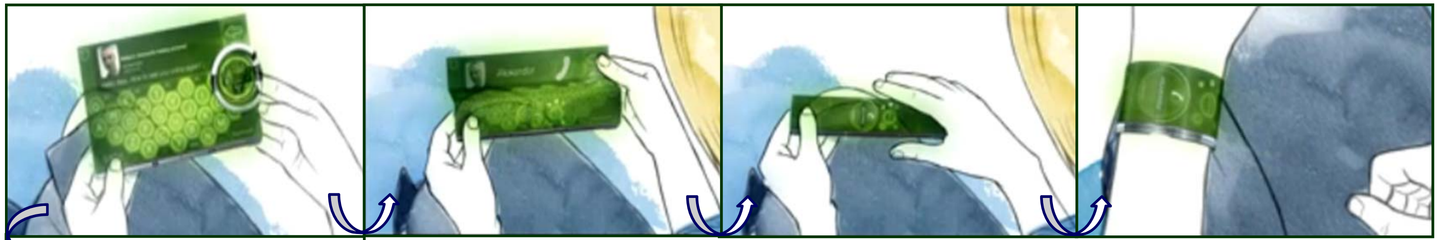
♣ Excellent charge/discharge efficiency

♣ Low Cost

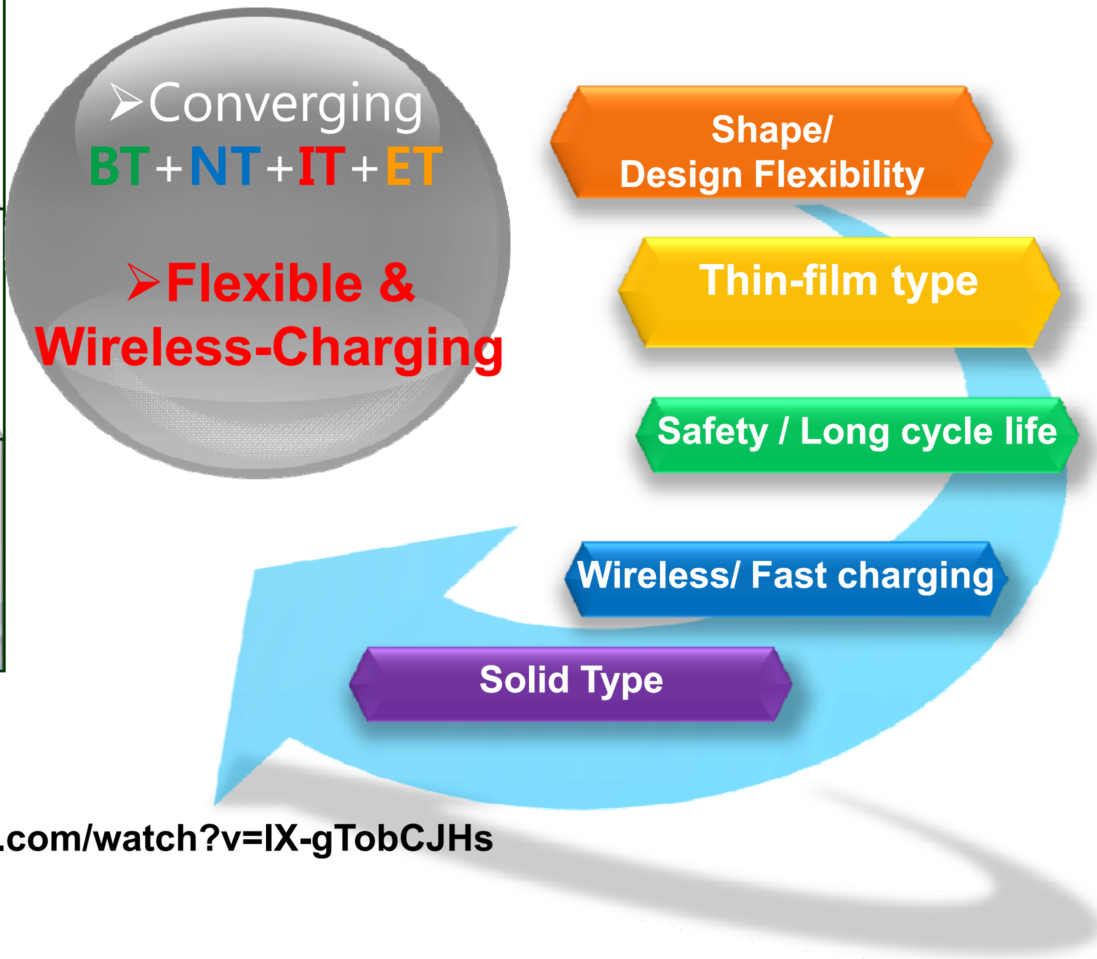
Small Size:
Diversity & specification of market
=> Rapid growth expected



Flexibility

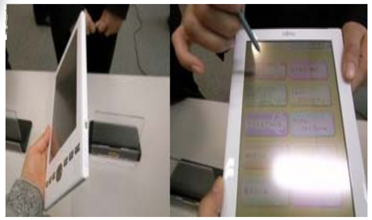



The Morph Concept
phone (Nokia)*



Flexible phone (Kyocera)

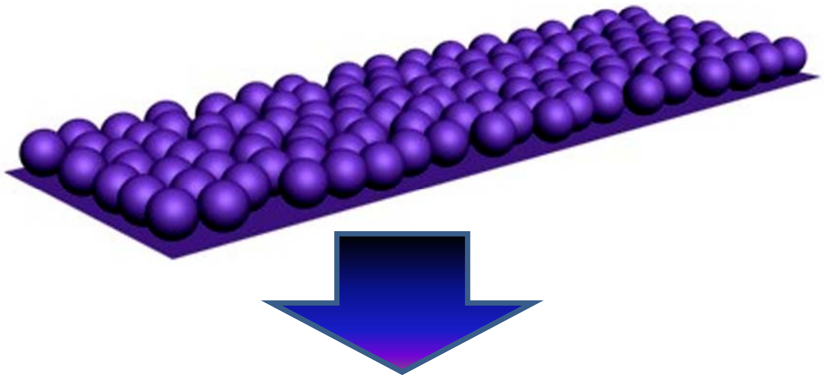
Flexible OLED (LG Display)



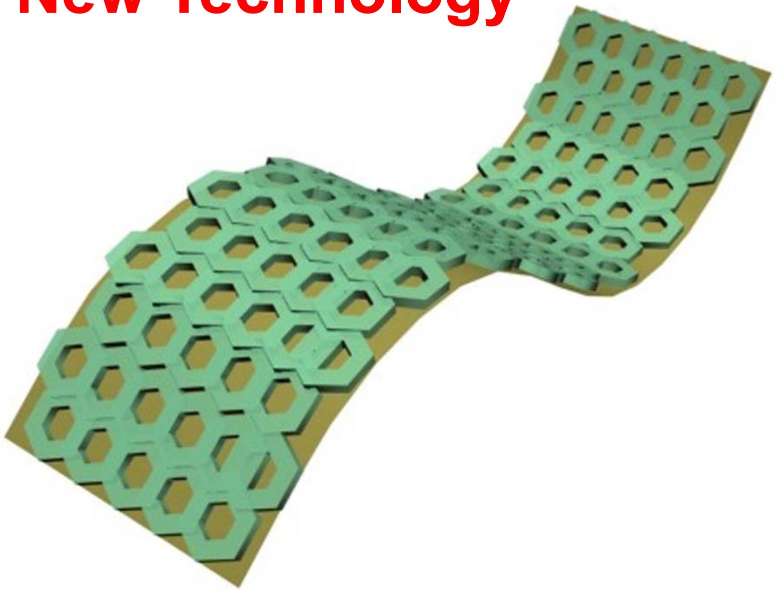
E-paper FLEPia (Fujitsu)

*http://www.youtube.com/watch?v=IX-gTobCJHs

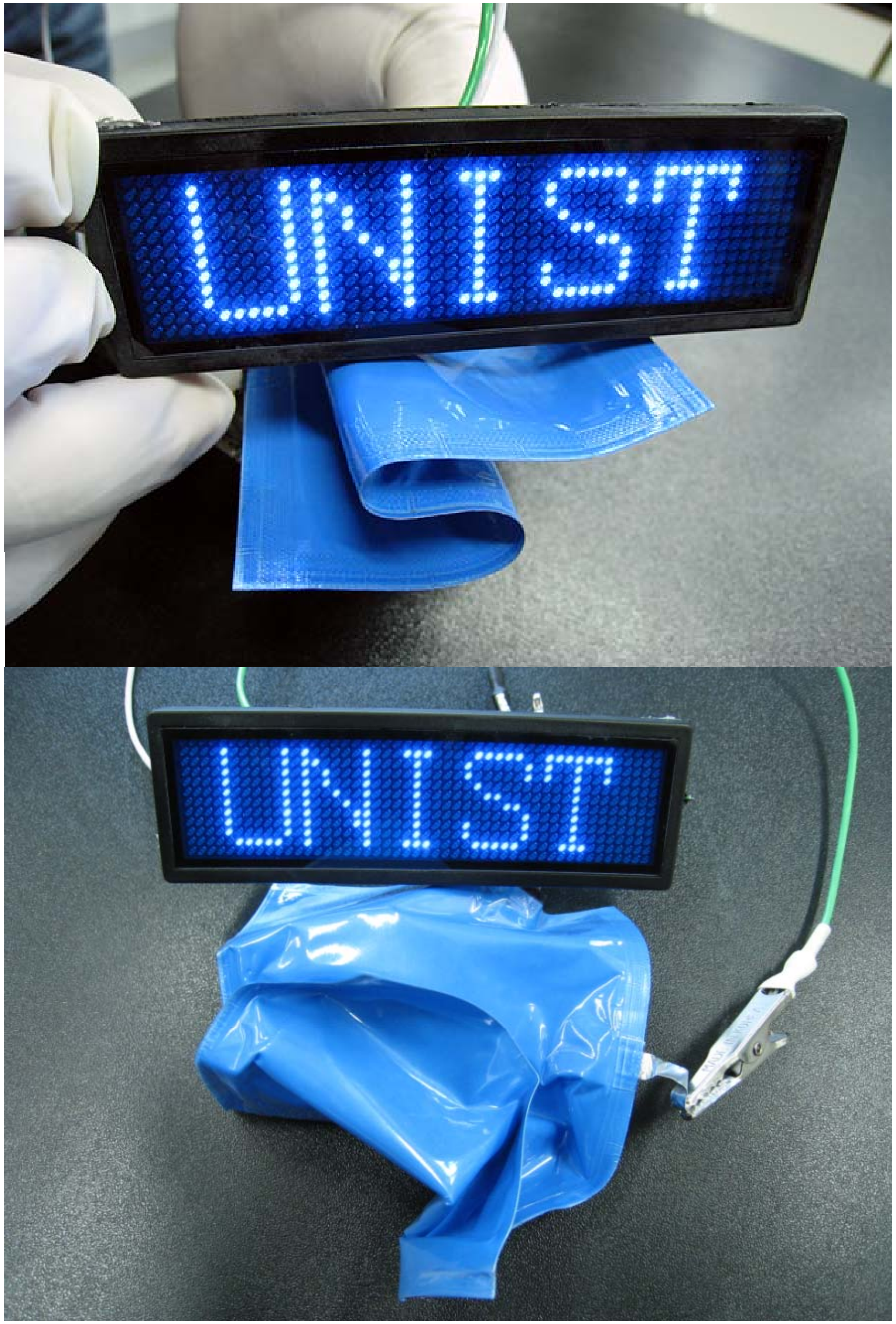
Current Technology



New Technology*



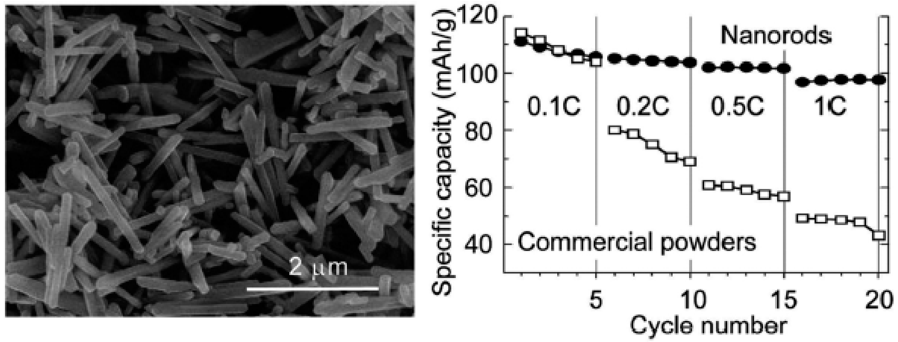
*<u>*Angew Chem. Int. Ed*</u>. 49, 2146, 2010
<u>*Adv. Mater.*</u> 22, 415, 2010



Requirements for Electrode Materials

◆ Cathodes

- ➢ Electrode density
- ➢ Cycle life
- ➢ Structural stability (thermal stability)
- ➢ Fast charging capability

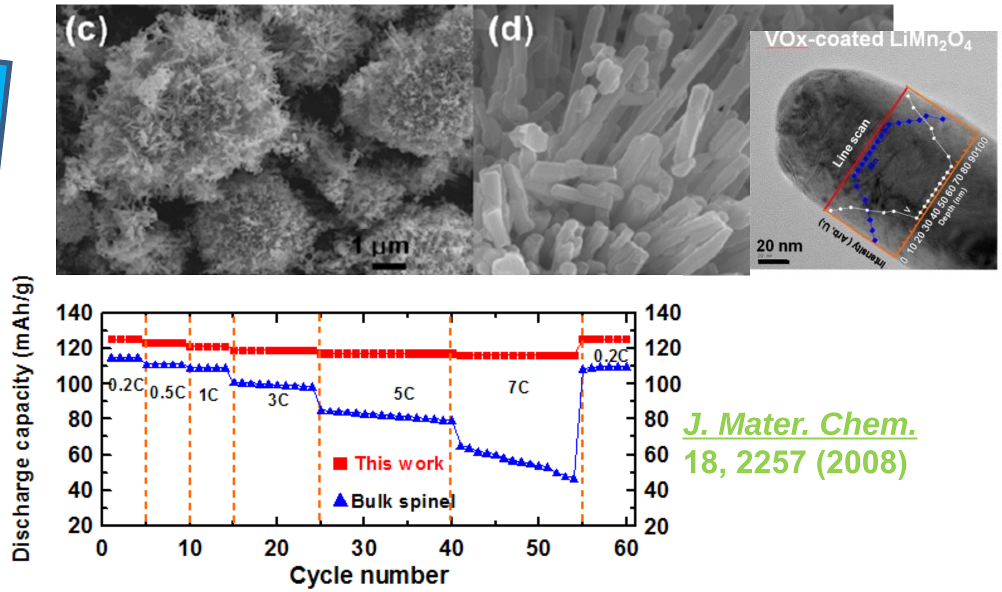


Cui et al. *Nano Lett.* 8, 3948 (2008)

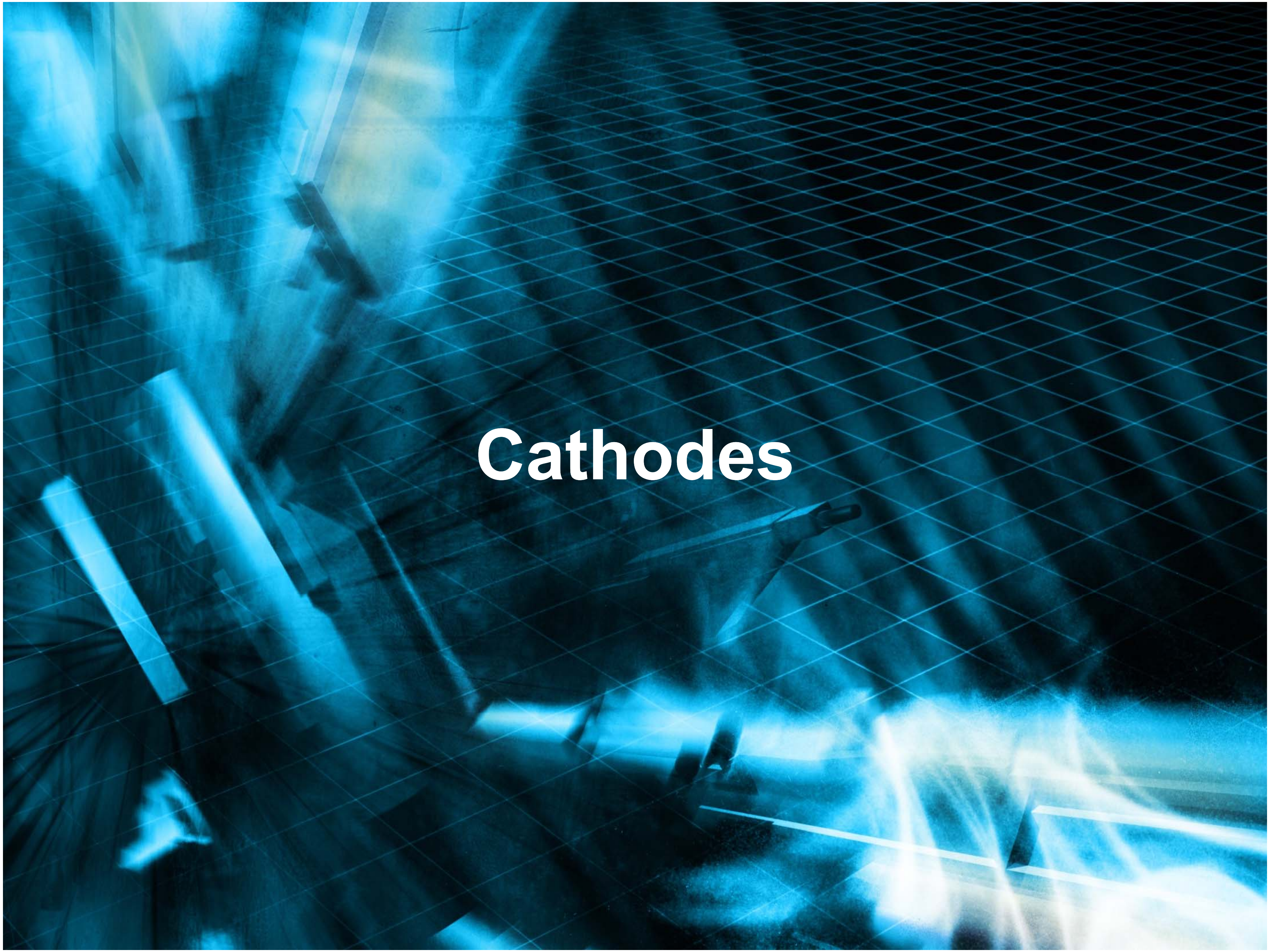
Nanoclustered Morphology

◆ Anodes

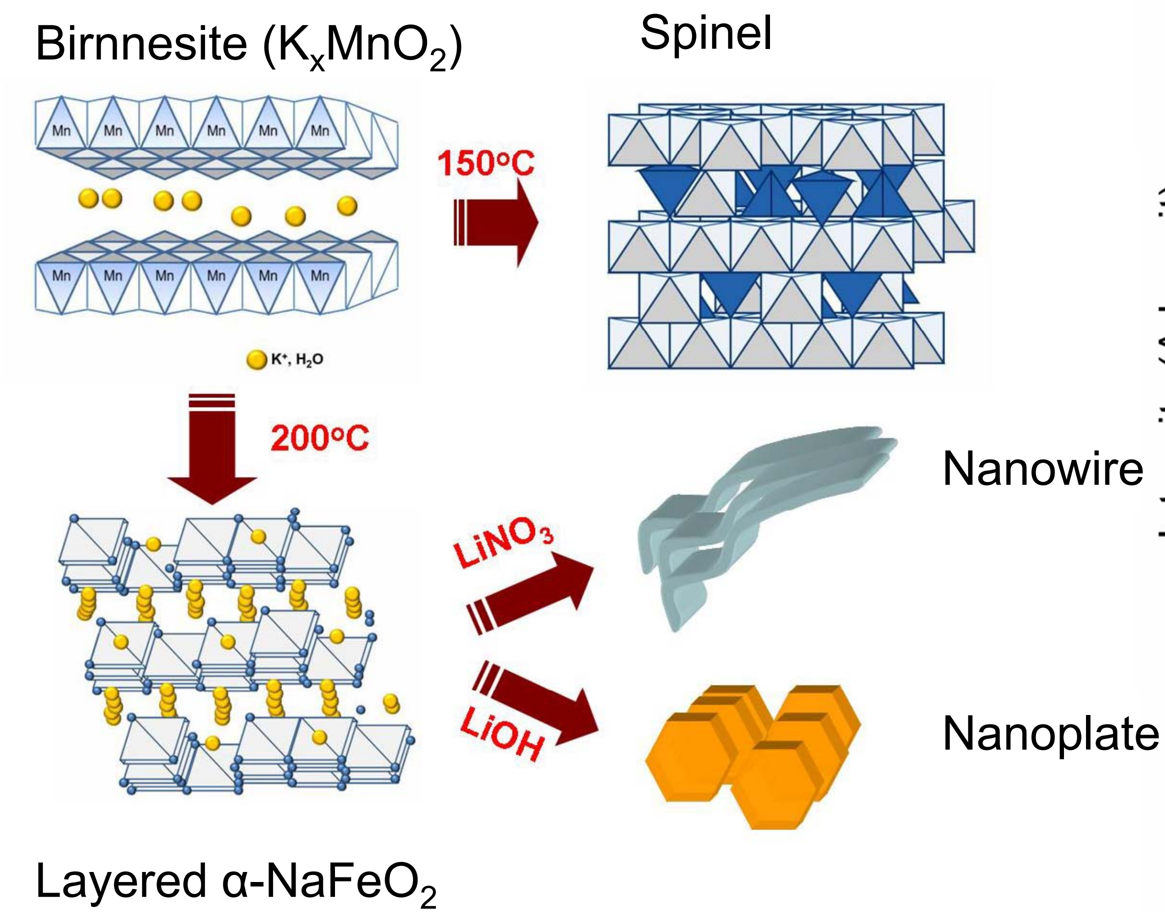
- ➢ Electrode density
- ➢ Cycle life
- ➢ Fast charging capability
- ➢ Volume expansion (<15%)
- ➢ Side reactions with electrolytes

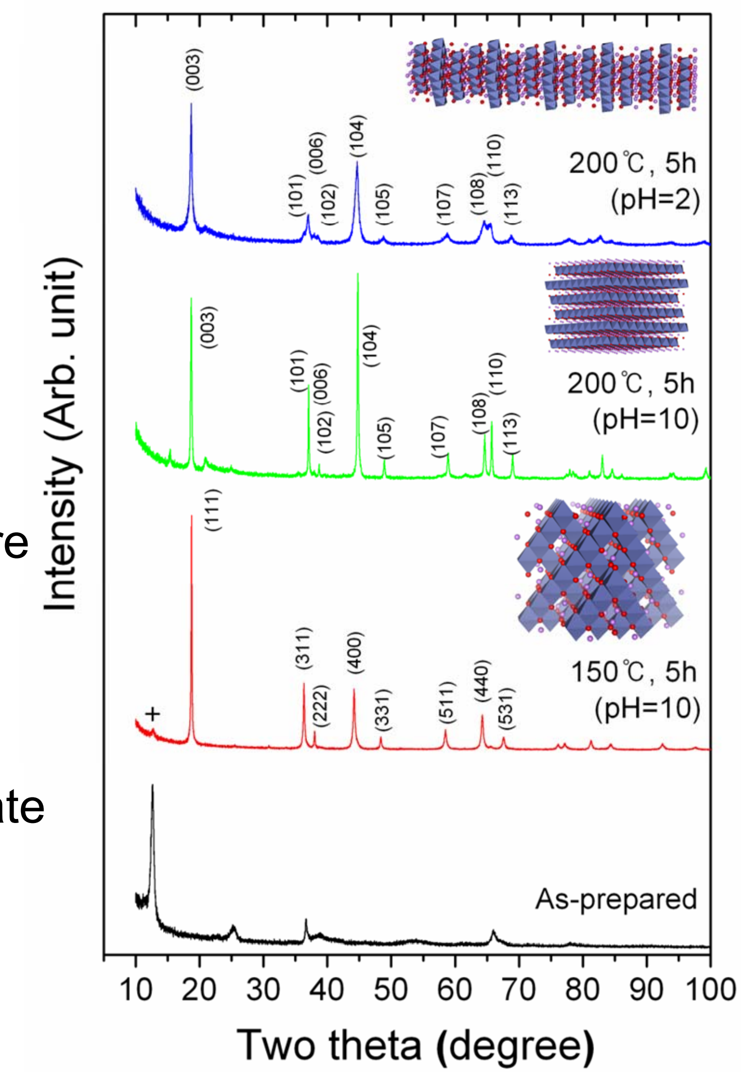


J. Mater. Chem. 18, 2257 (2008)


Cathodes

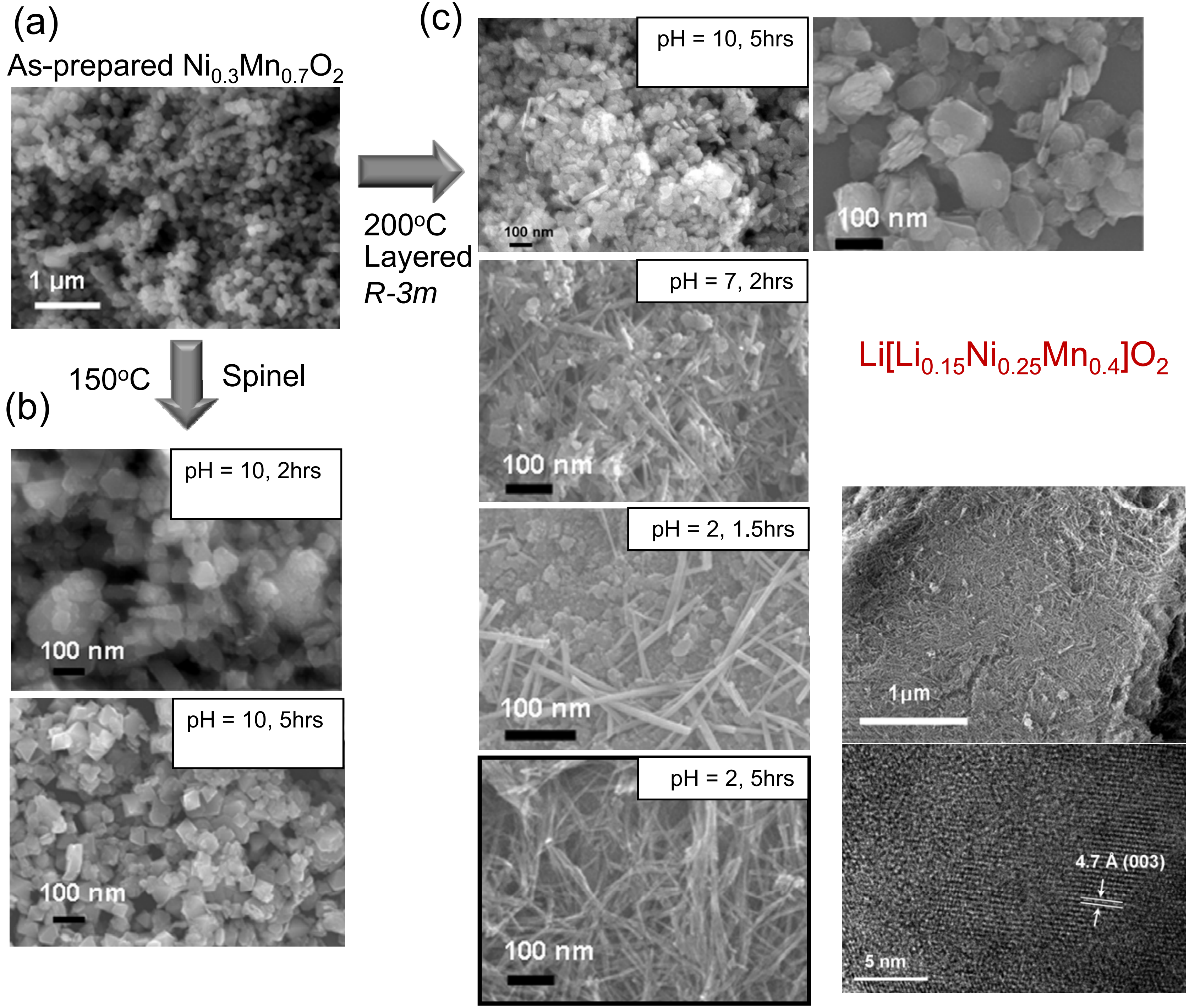
Lithium Rich Layered Materials





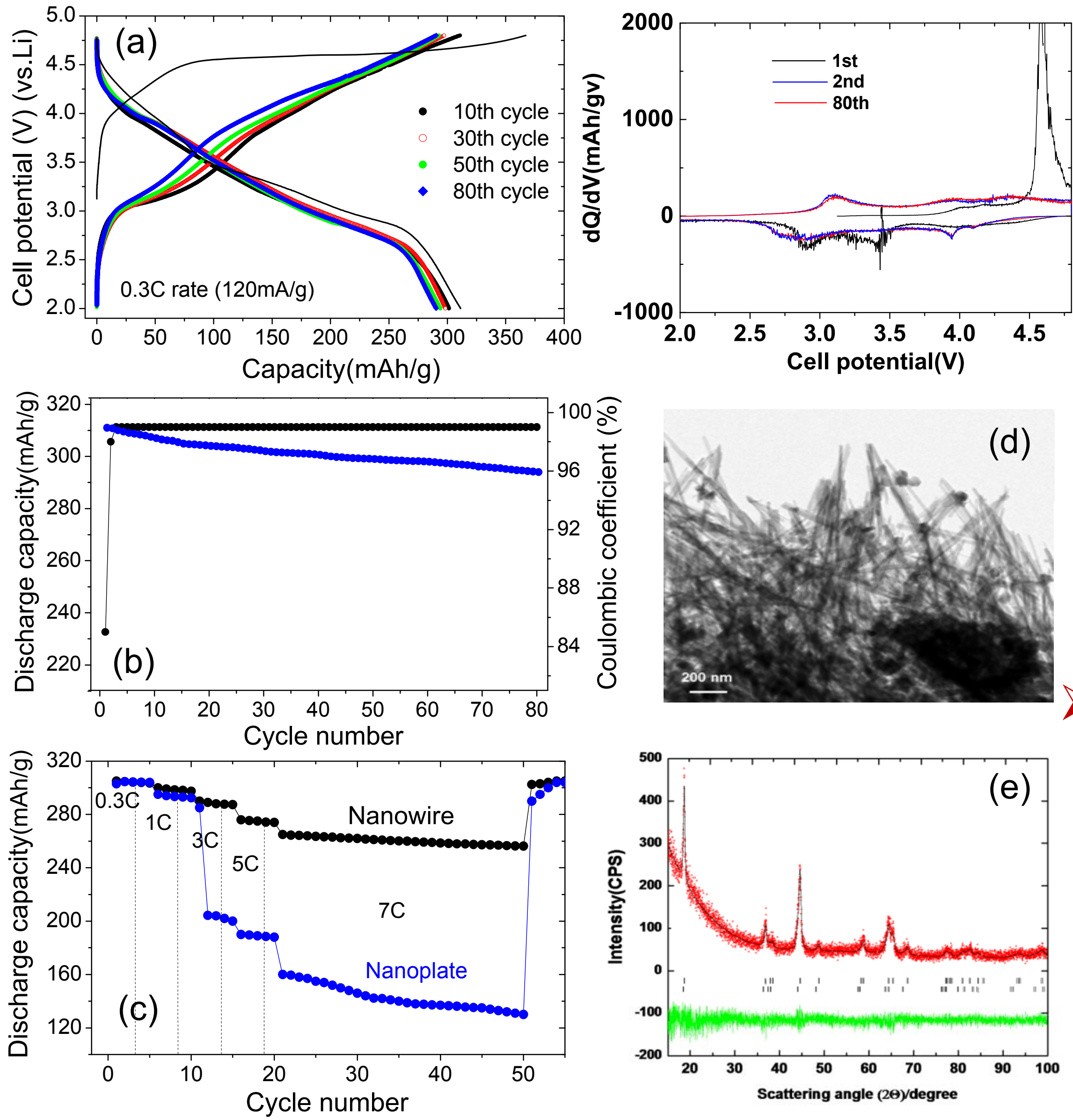
Nano Lett. 8, 957(2008)

Chem. Commu. 218 (2009)



(a)
As-prepared $Ni_{0.3}Mn_{0.7}O_2$
1 μm
150°C
Spinel
(b)
pH = 10, 2hrs
100 nm
pH = 10, 5hrs
100 nm
(c)
200°C
Layered
R-3m
pH = 10, 5hrs
100 nm
100 nm
pH = 7, 2hrs
100 nm
pH = 2, 1.5hrs
100 nm
pH = 2, 5hrs
100 nm
$Li[Li_{0.15}Ni_{0.25}Mn_{0.4}]O_2$
1μm
4.7 Å (003)
5 nm

Cycling Results



- (d and e) after cycling

Anodes

Candidates

H																	He
Li	Be											B	**C**	N	O	F	Ne
Na	Mg											**Al**	**Si**	**P**	**S**	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	**Zn**	**Ga**	**Ge**	As	Se	Br	Kr
Rb	Sr	Y	Zr	**Nb**	**Mo**	Tc	Ru	Rh	Pd	Ag	Cd	In	**Sn**	**Sb**	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	**Bi**	Po	At	Rn
Fr	Ra	Ac															

Lithium reaction mechanisms

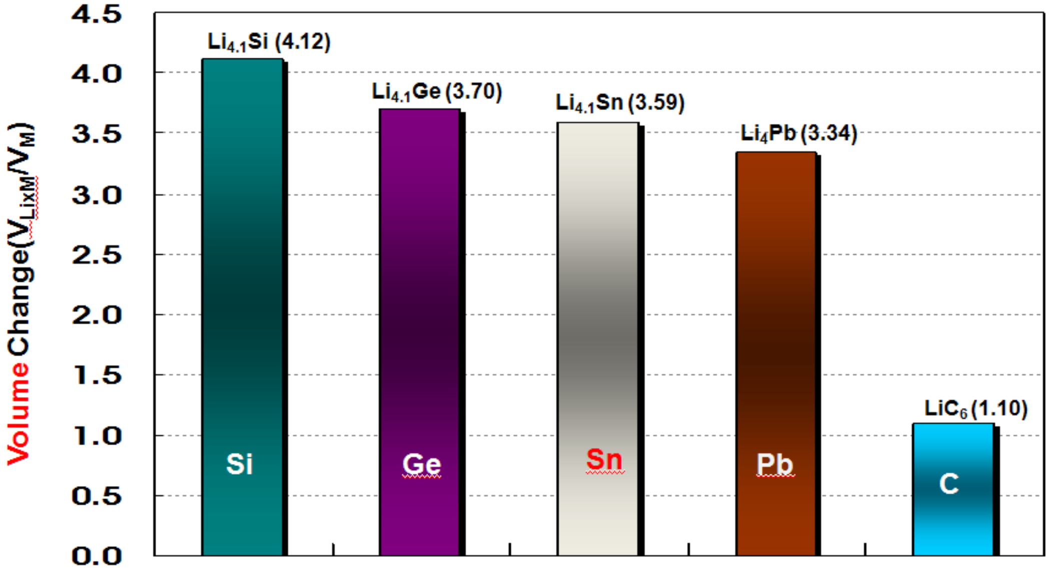
1) **Sn, Ge, and Si: $M + xLi^+ + xe^- \leftrightarrow Li_xM$**
2) **$SnO_2 + 4Li^+ + 4e^- \rightarrow Sn + 2Li_2O$ (1)**

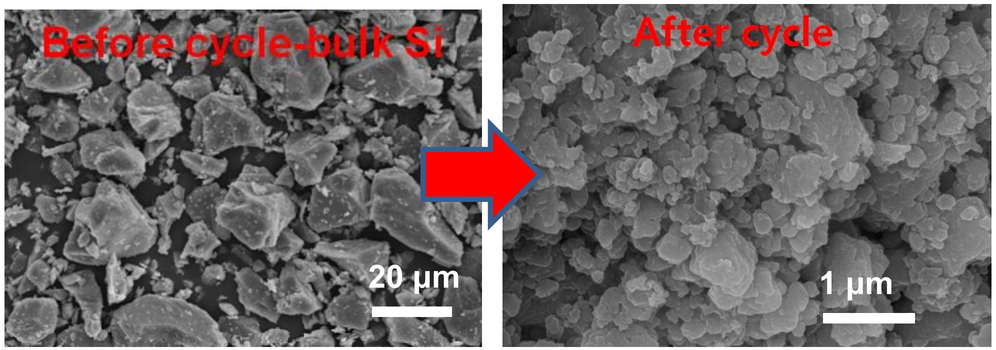
   $Sn + xLi^+ + xe^- \leftrightarrow Li_xSn$ $(0 \leq x \leq 4.4)$ (2)
3) **$M^{II}O + 2Li^+ + 2e^- \leftrightarrow Li_2O + M^0$ (3d transition metal oxide)**
4) **$MP_n \leftrightarrow Li_xMP_n$ (Li-intercalation) (1)**

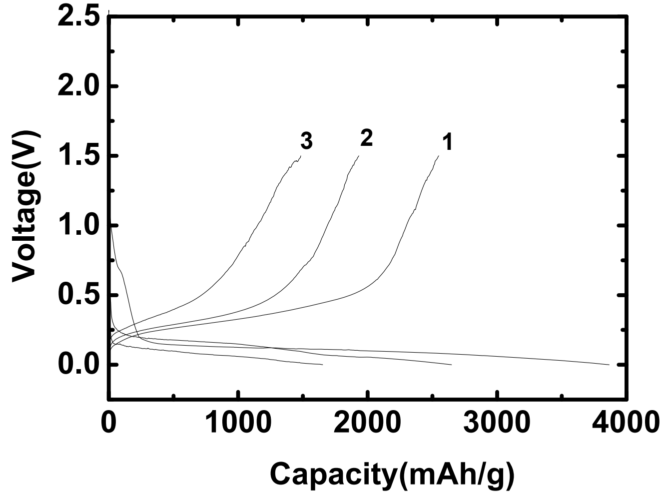
   $MP_n \leftrightarrow M\ (Li_xM) + Li_xP$ (metallization or metal alloying) (2)

Volume change issue

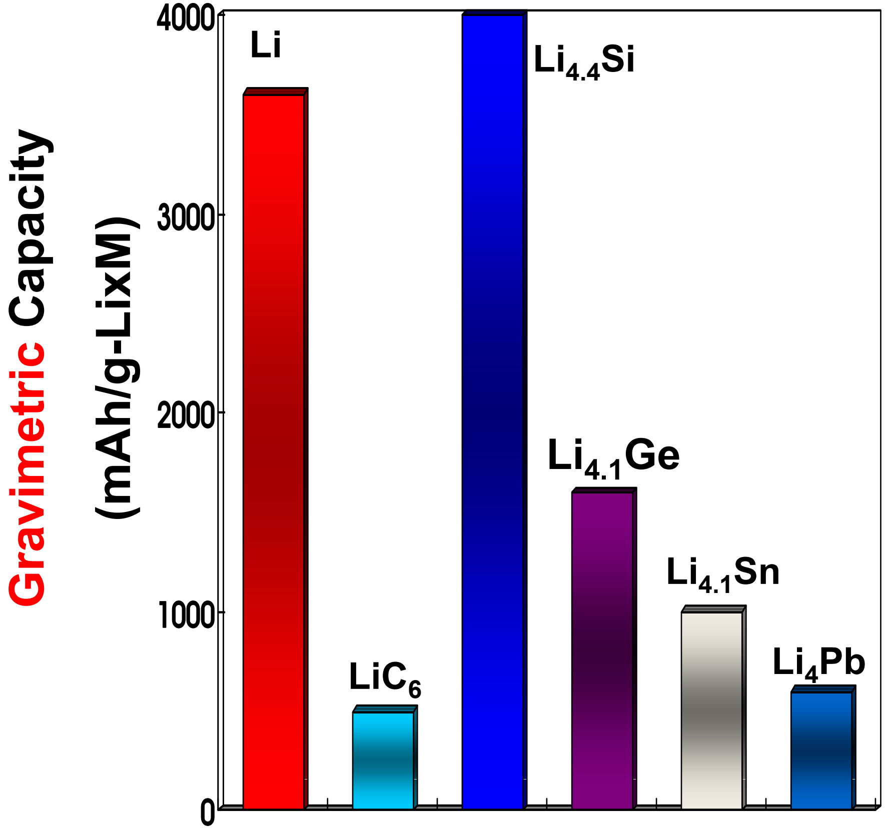
- Particle pulverization and isolation from the Cu collector
  → Rapid capacity fade

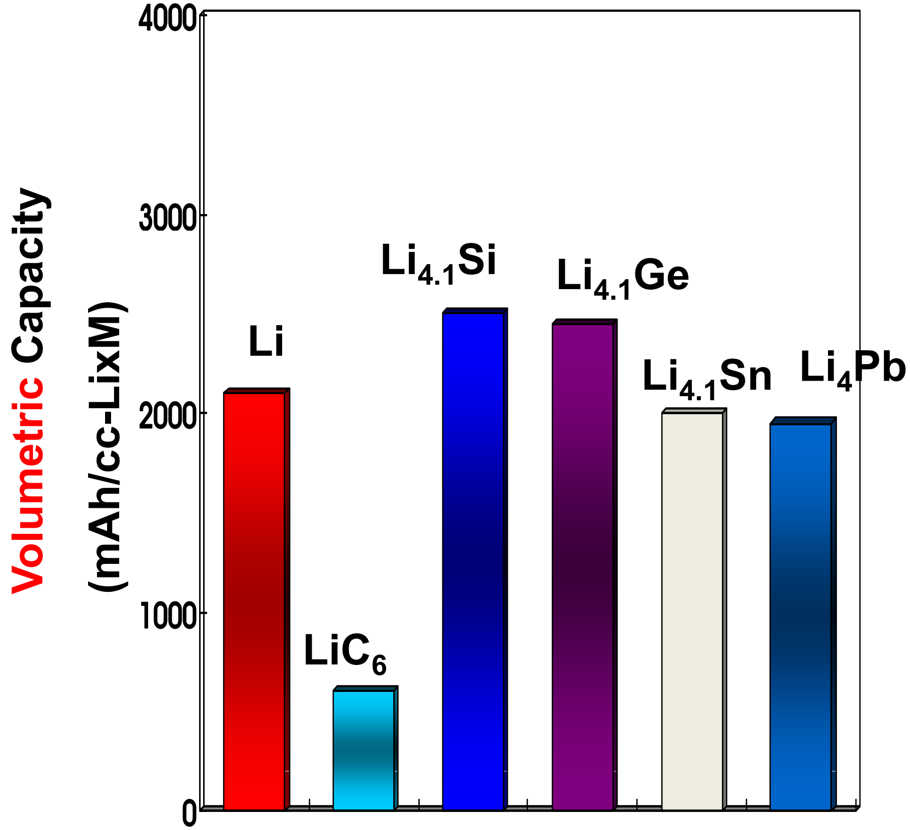






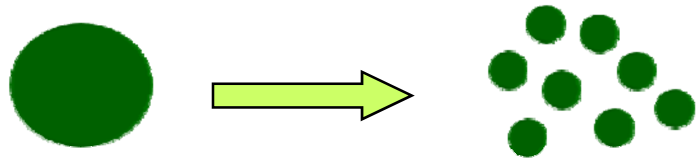
Gravimetric vs. Volumetric capacity



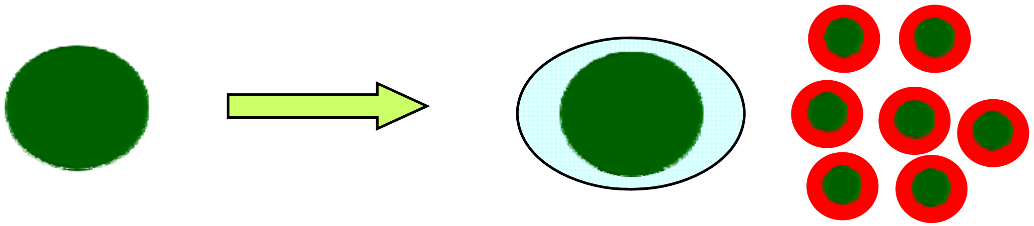


Strategies*

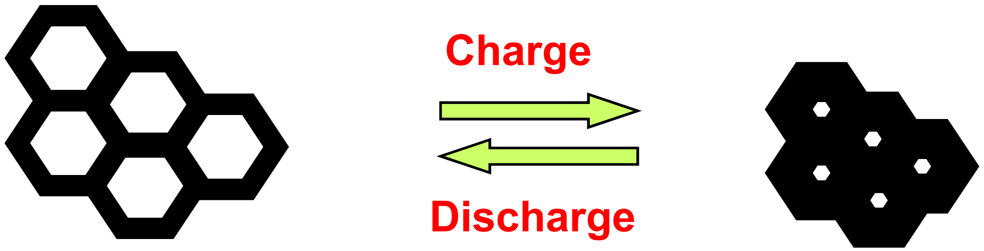
- Control of particle size (uniform dispersion)



- Formation of dimensionally stable coating layer



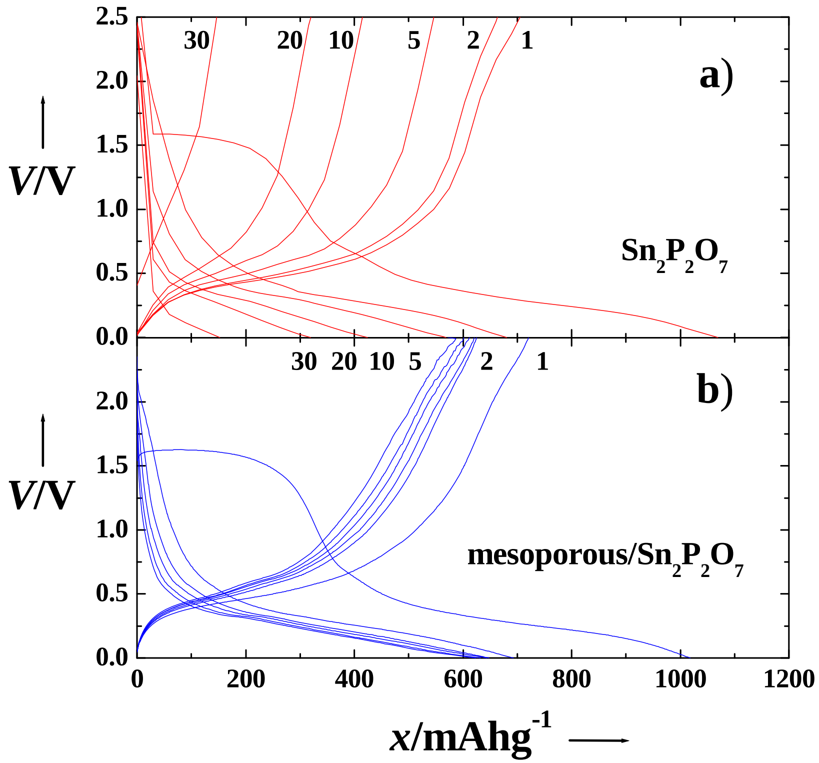
- Artificial formation of “Buffer Zone” so as to alleviate volume change

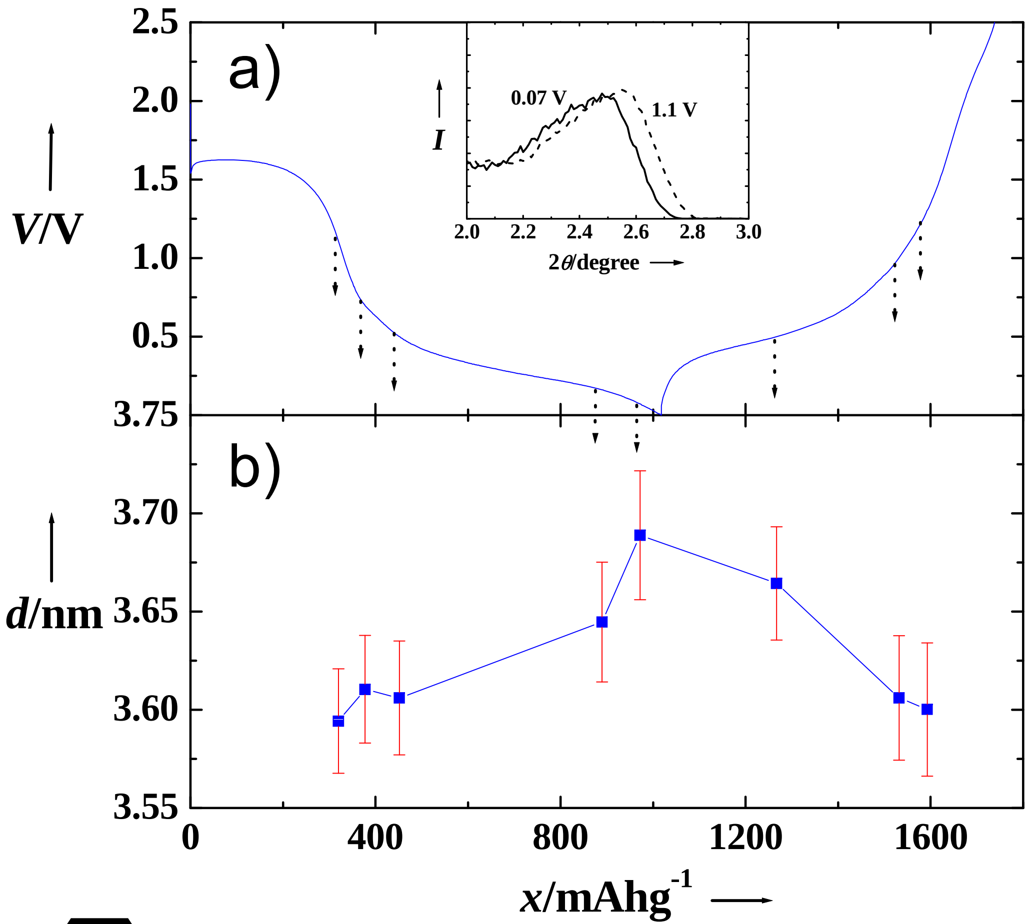


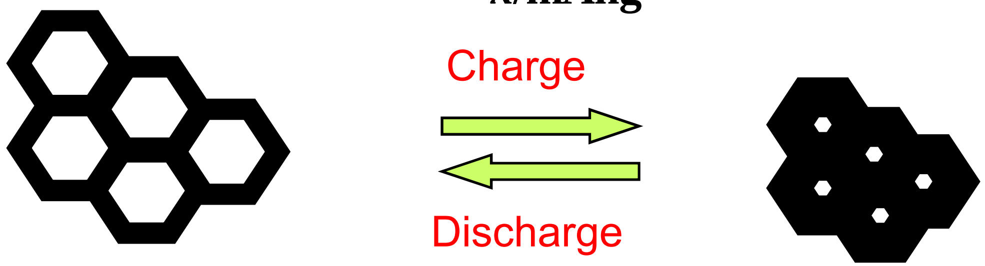
*Adv. Funct. Mater. 19, 1497, 2009, Feature article

Energy & Environ. Sci. 2, 181, 2009, Invited review article

Role of pores

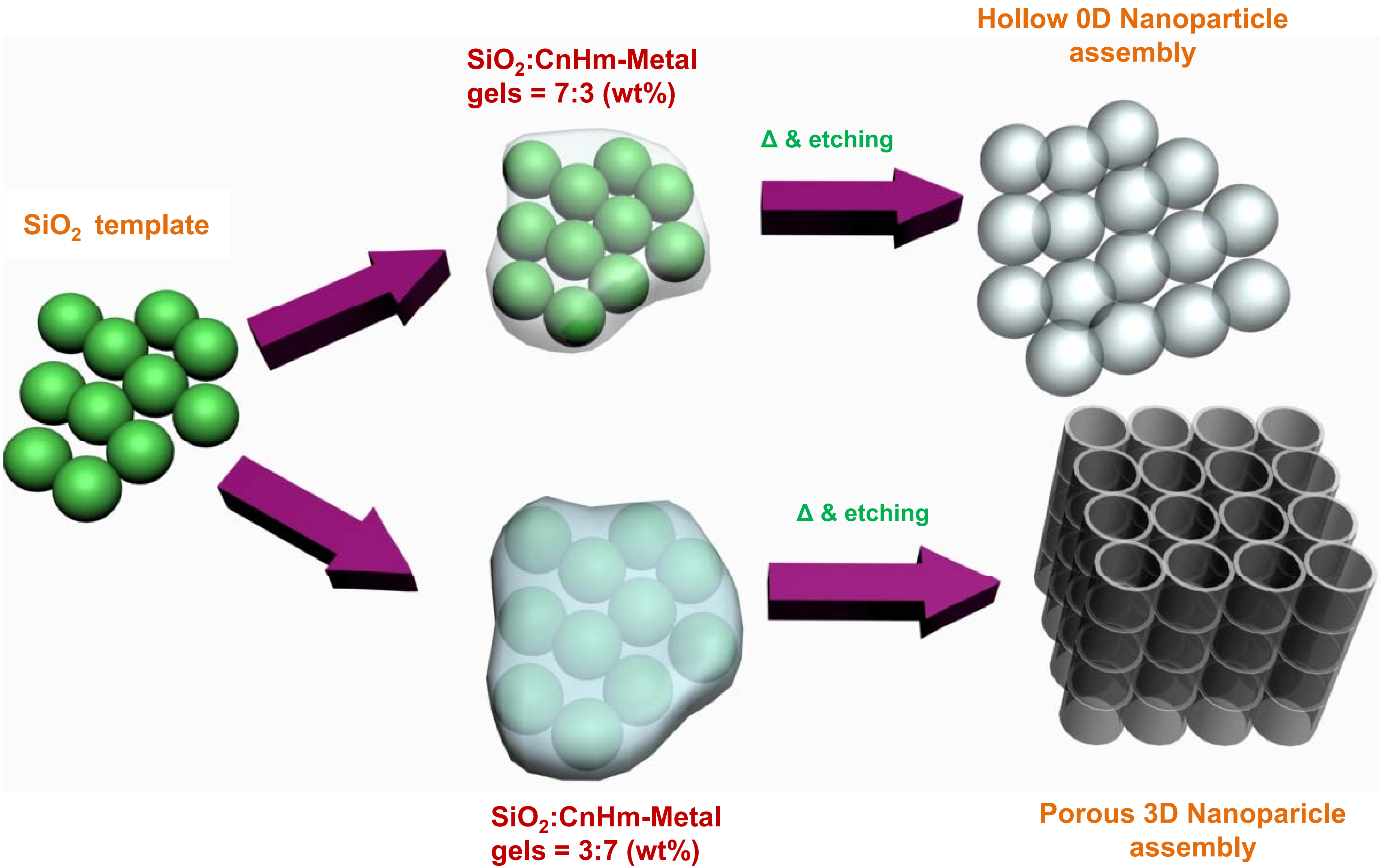




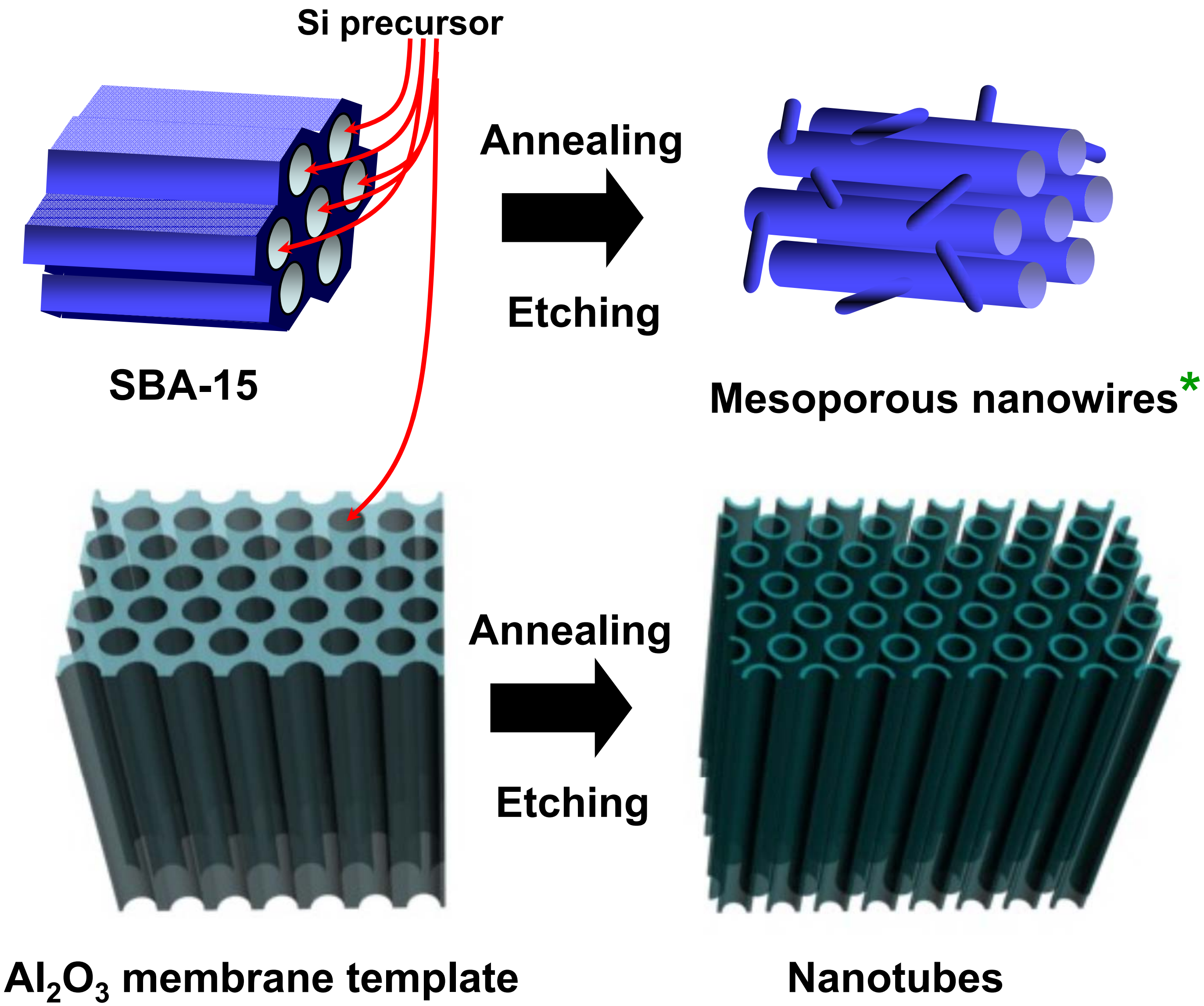


Angew. Chem. Int. Ed. 43, 5987 (2004)

Approaches

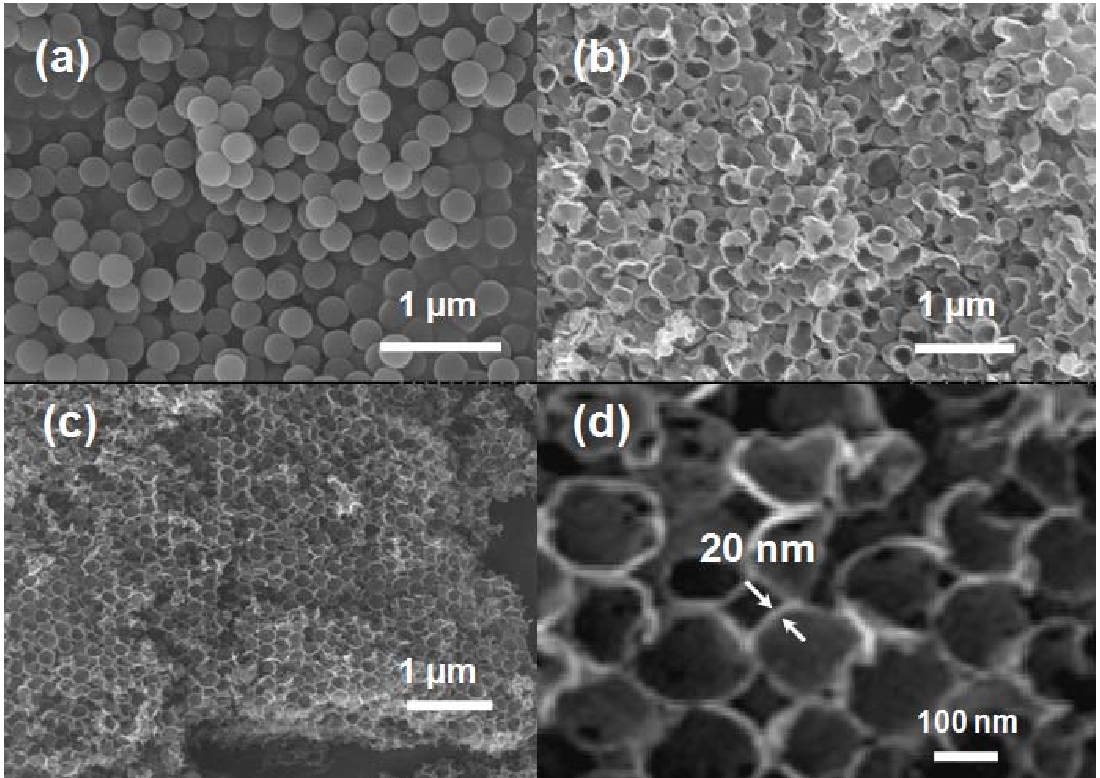


Hollow 0D Nanoparticle assembly
SiO_2:CnHm-Metal gels = 7:3 (wt%)
Δ & etching
SiO_2 template
Δ & etching
SiO_2:CnHm-Metal gels = 3:7 (wt%)
Porous 3D Nanoparicle assembly

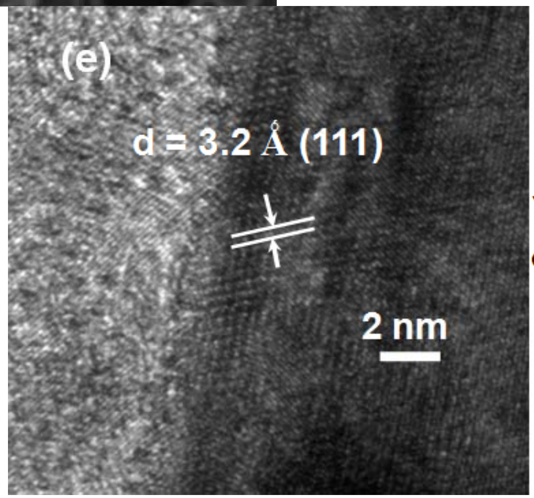


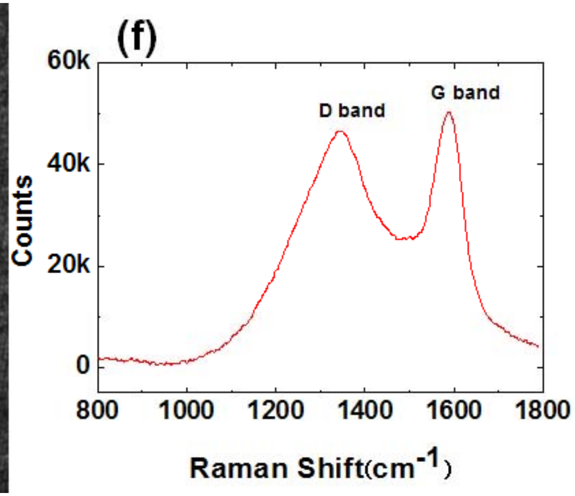
*Nano Lett. 8, 3688 (2008)

0D & 3D Ge porous particles*



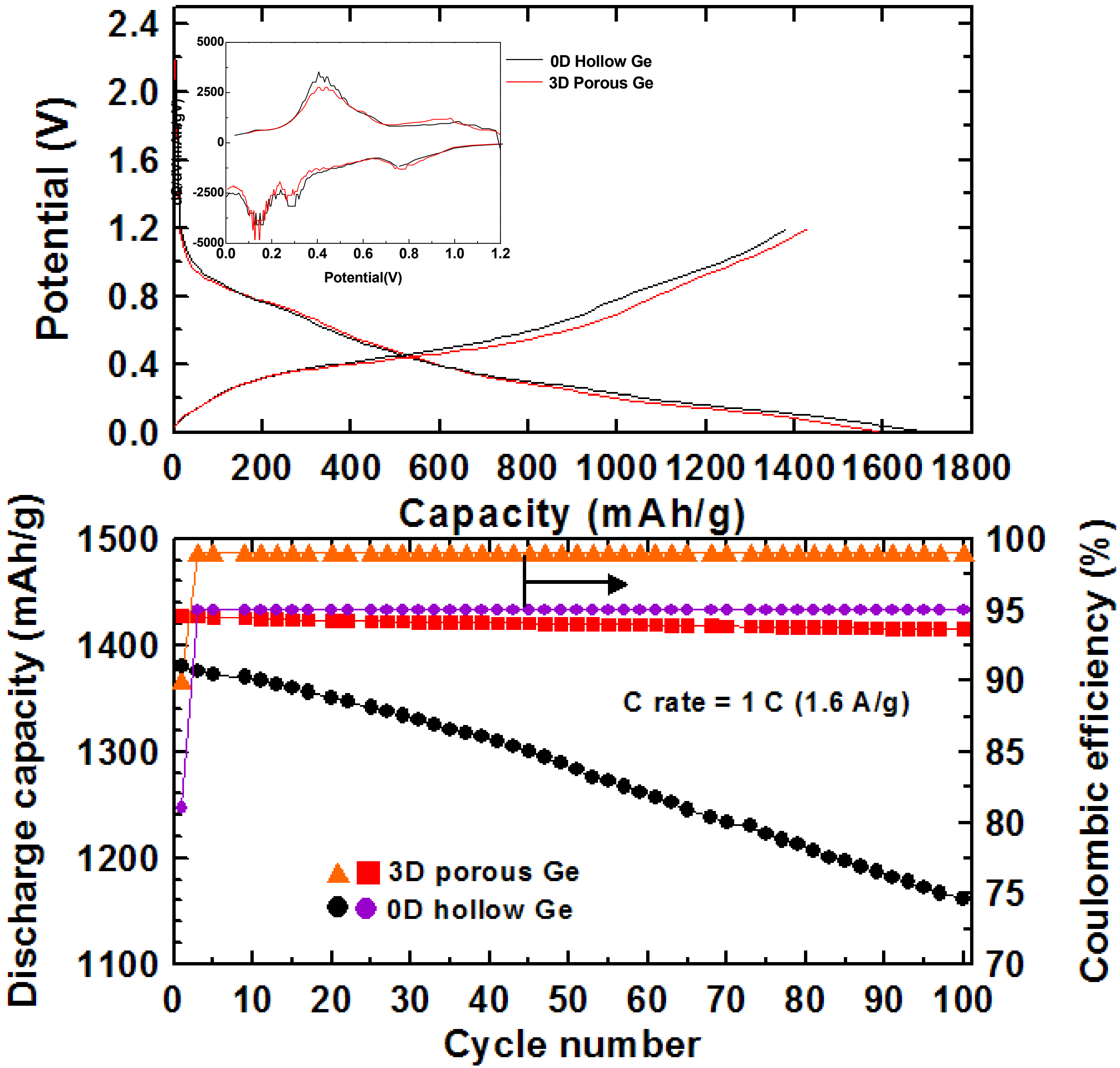
(a) silica template, (b) 0D hollow Ge nanoparticle assembly,
(c) 3D porous Ge nanoparticle assembly,
(d) is expanded image of (c),
(e and f) high resolution TEM image and Raman spectrum



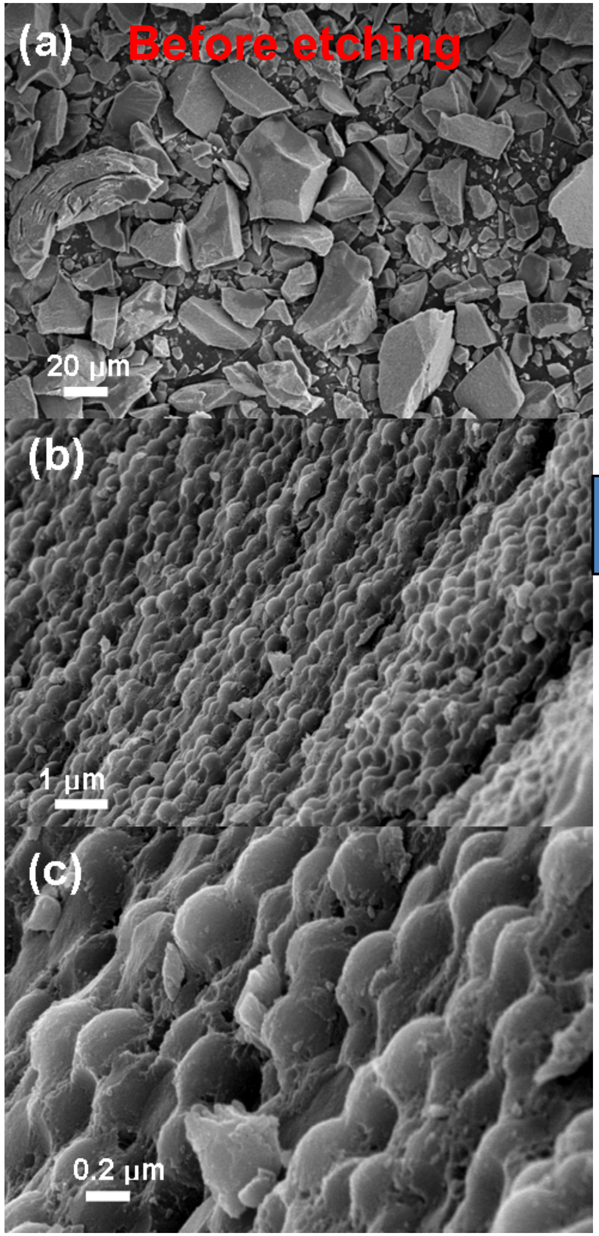


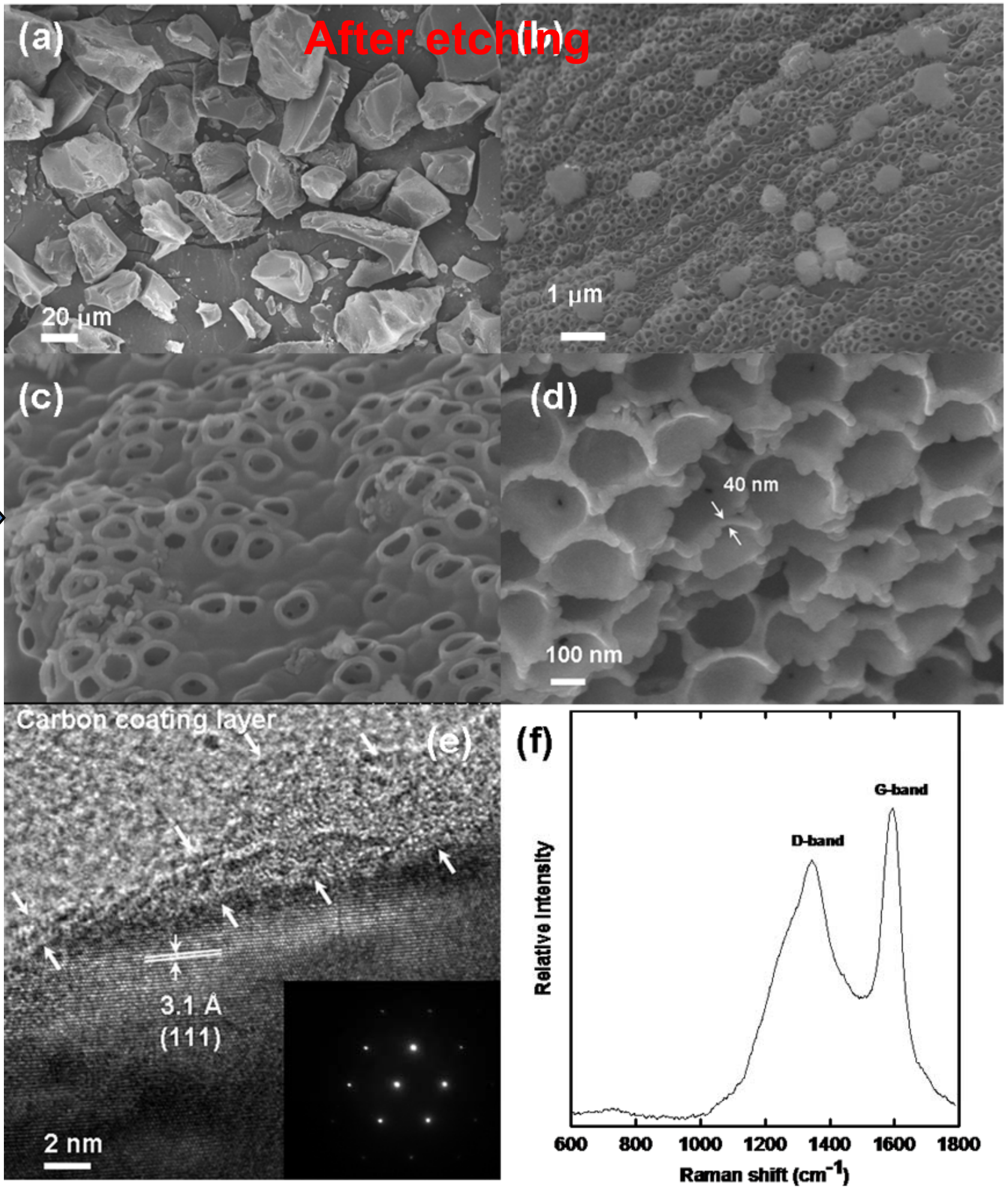
Adv. Mater. 22, 415, 2010

0D & 3D Ge porous particles – cycling result



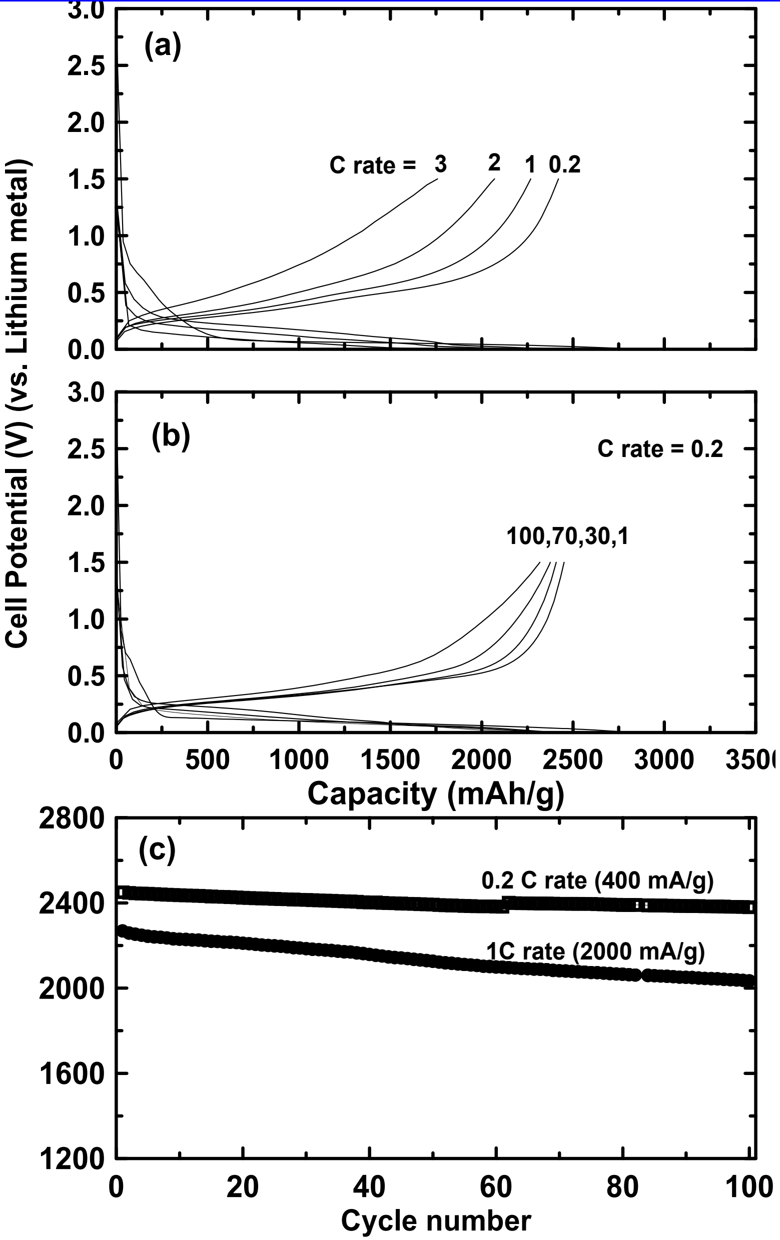
3D Porous Si Particles



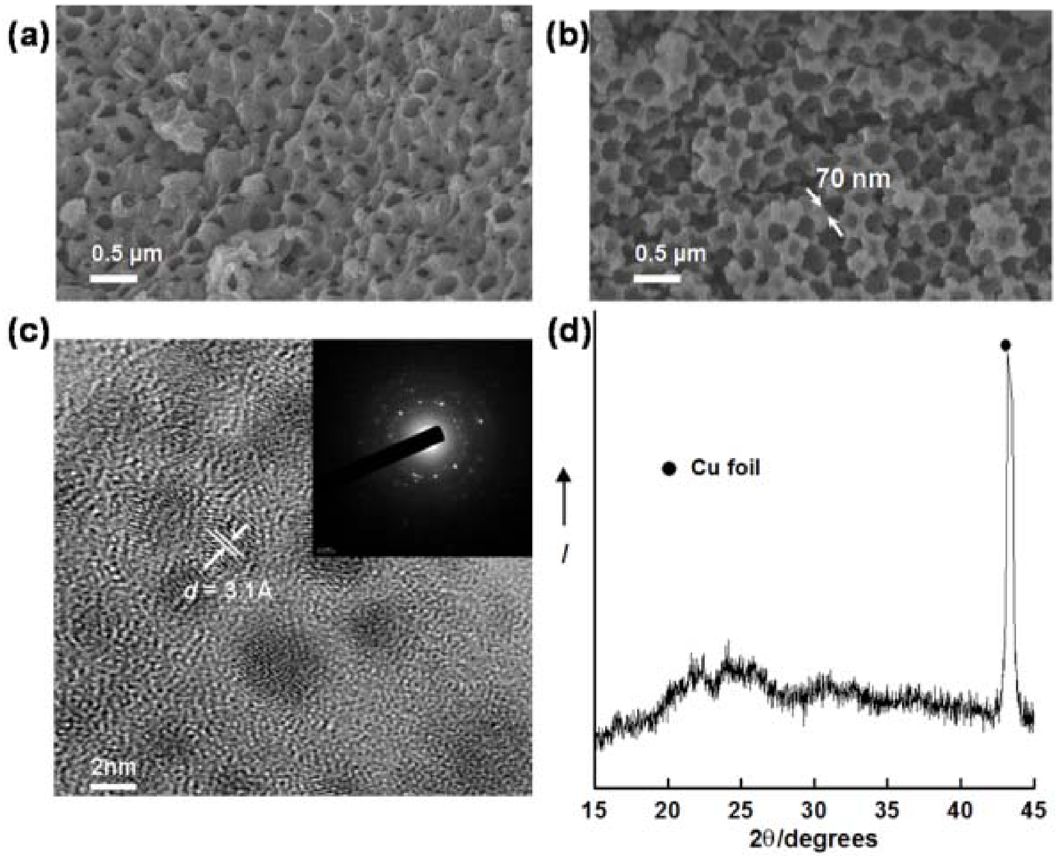


Angew. Chem. Int. Ed., 47, 10151 (2008) (HOT article)

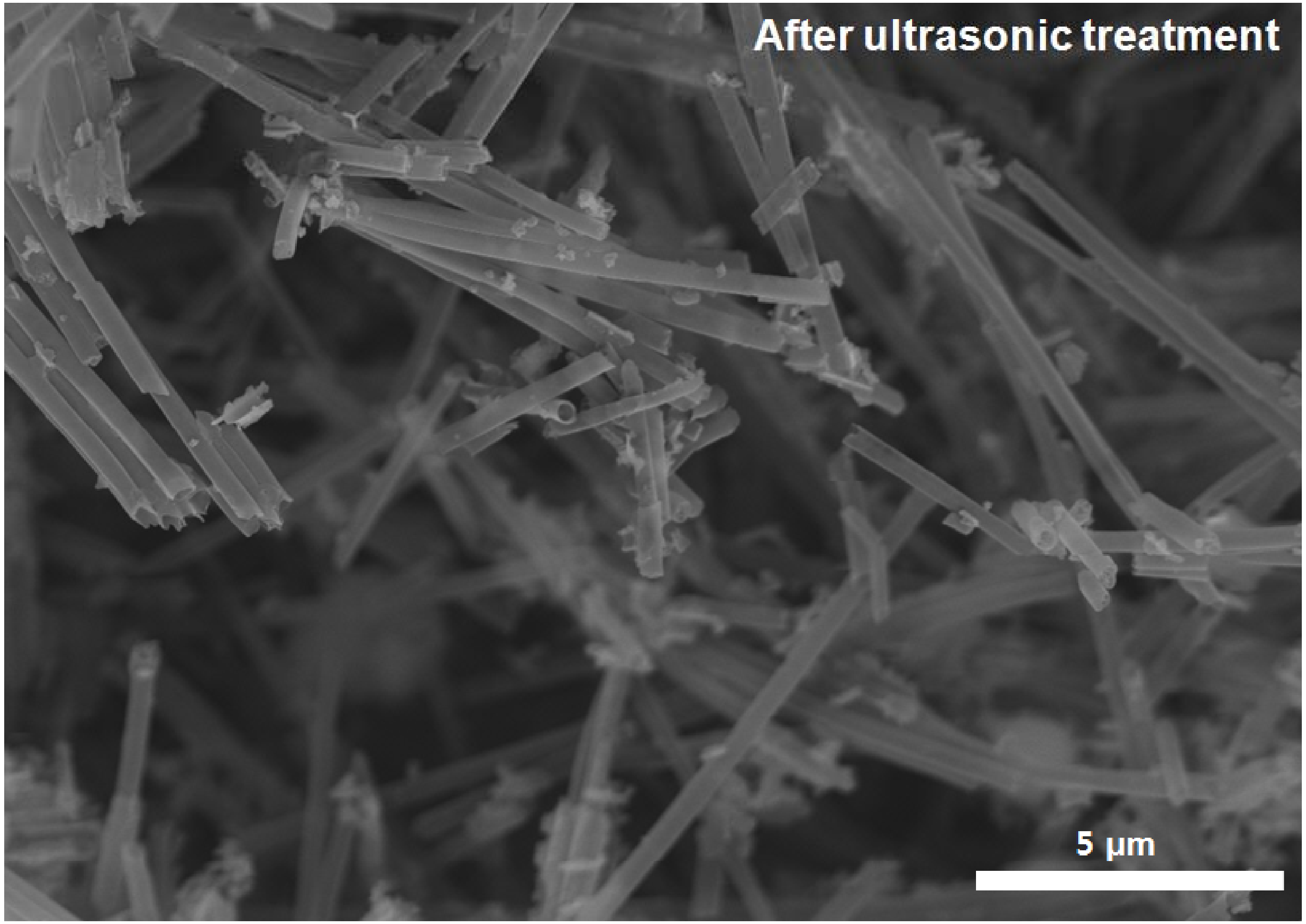
Cycling results



Ex situ TEM



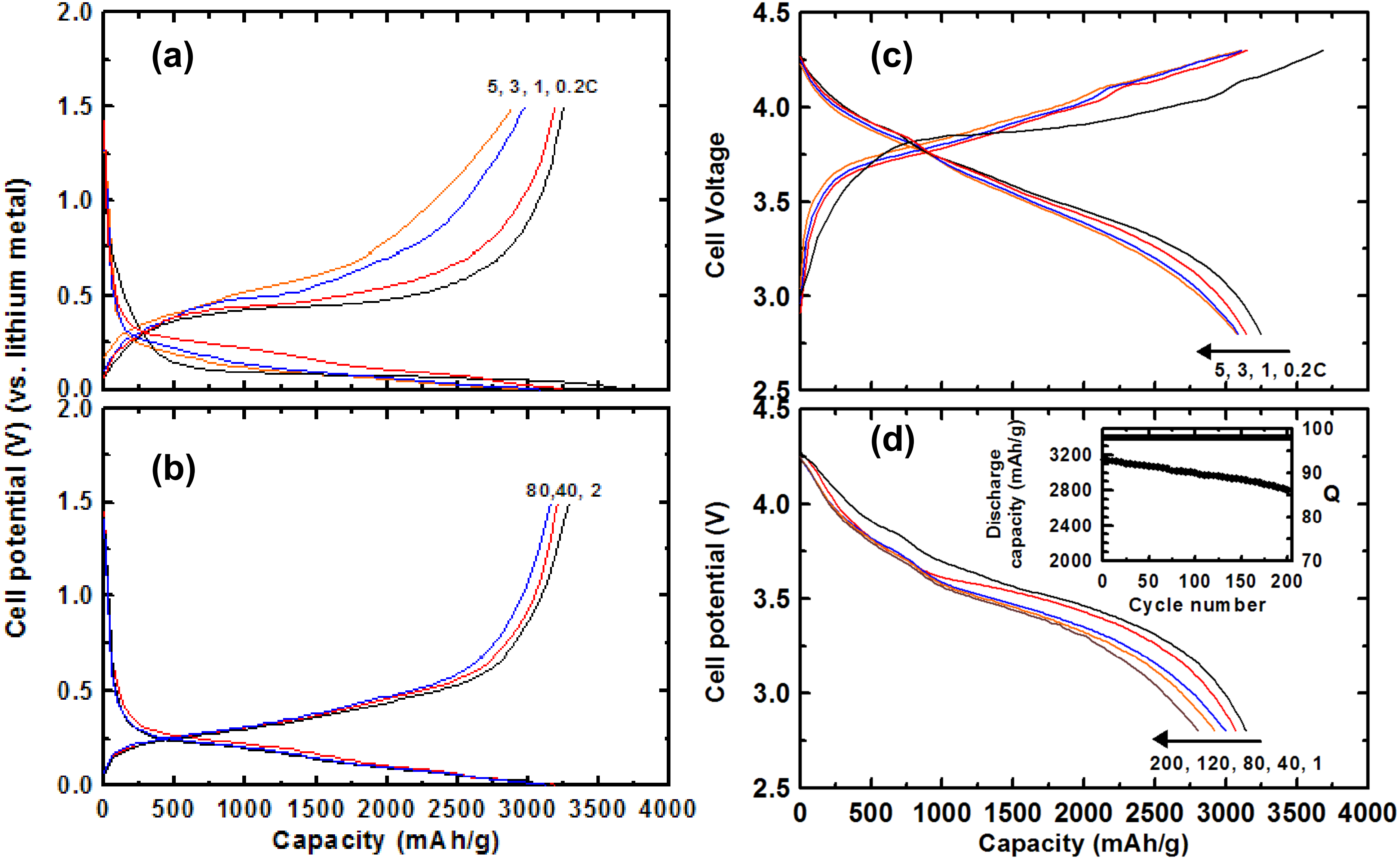
Si nanotubes



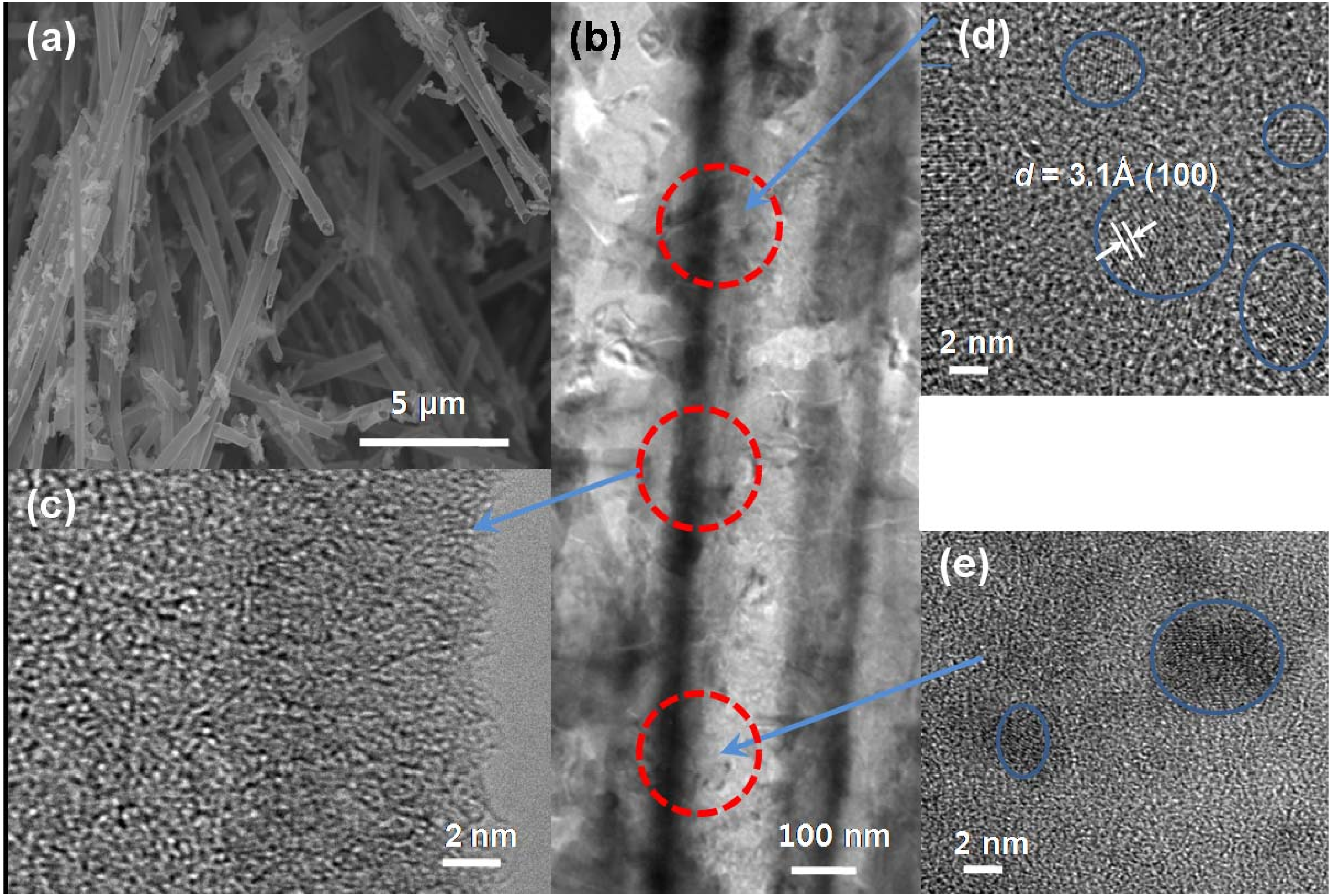
**Nano Lett. 9, 3844, 2009*

Highlighted in Nature Nanotech., Nature Mater. in Asia & MIT Technical Review

Si nanotubes- Half and full cell tests



Si nanotubes- Ex-situ TEM



Summaries

- **In the case of the metallic anode nanomaterials, there has been growing researches for reducing the critical volume changes by phase transition during lithium reaction.**

- **The nanoscaled synthetic methods for bulk with 3D pores, and nanotube structures demonstrated meaningful solutions for the control of the volume expansion.**

- **Mostly important, if considering the volumetric energy denisty, bulk with tailored porosity will be the best choice for Li-ion battery anodes.**

Acknowledgements

Converging Research Center and WCU programs by MEST & NRF