上海交通大學
SHANGHAI JIAO TONG UNIVERSITY

Design and Development of Novel Materials for Advanced Lithium Ion Battery

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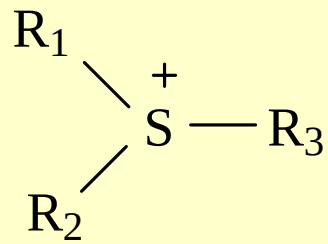
1 New Ionic Liquids (ILs) Electrolytes

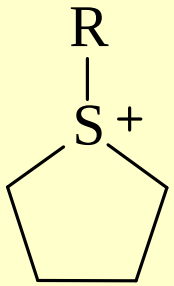
- Asymmetric sulfonium ILs
- Dicationic ILs
- Guanidinium ILs
- Diether-functionalized Ammonium ILs

Structures of asymmetric sulfonium ILs

Cations:

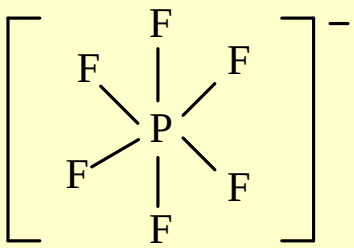


trialkylsulfonium

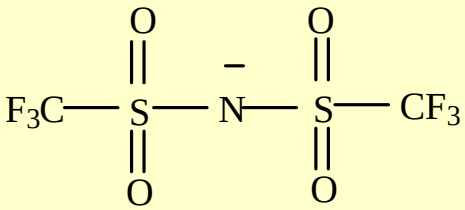


cyclic-sulfonium

Anions:



PF_6^-



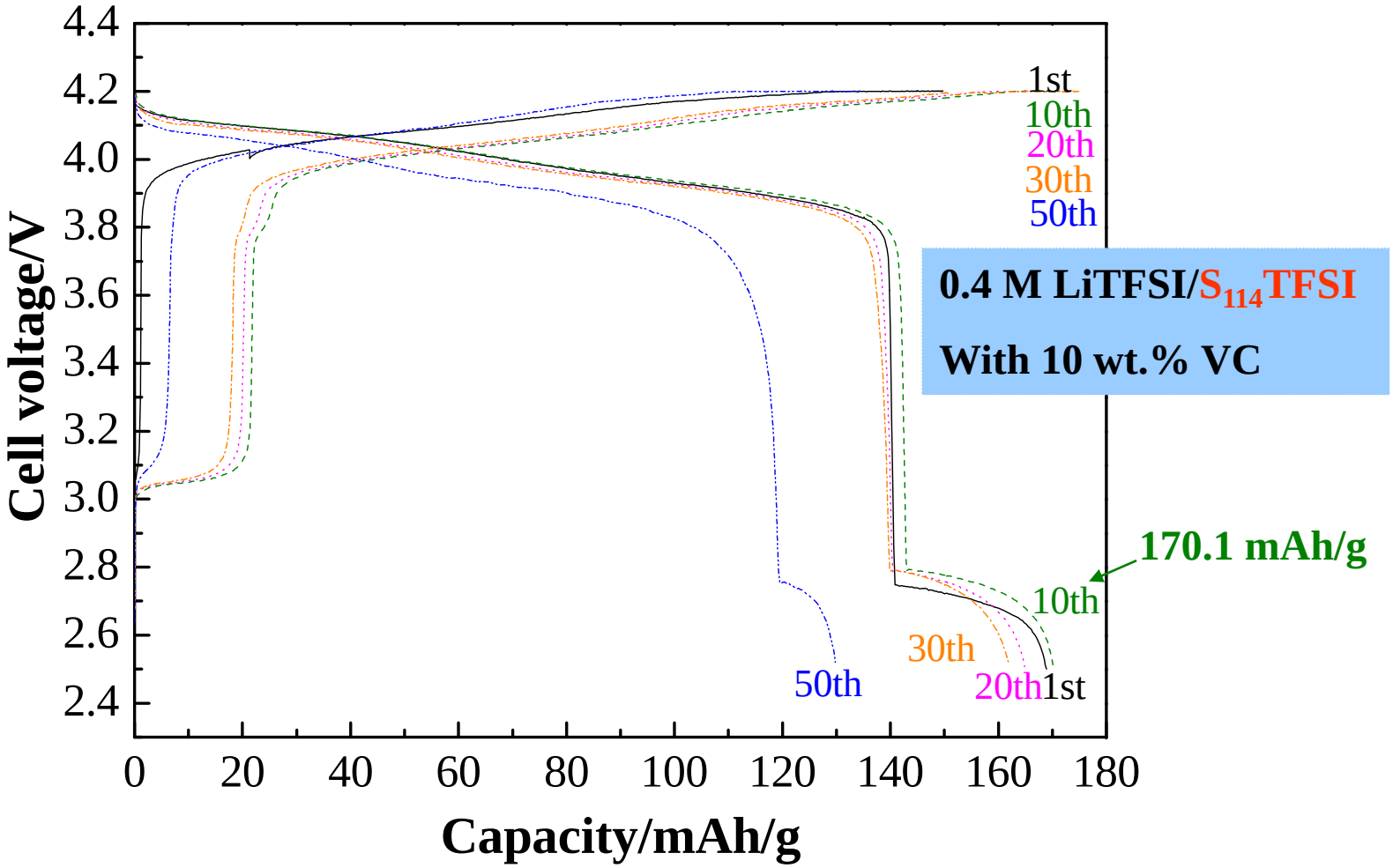
$TFSI^-$

Li Yang*, Zhengxi Zhang, *etal, Journal of Power Sources, 162, 614-619, (2006)*
Li Yang* , Yaju Guo, *Journal of Power Sources,* 156, 555-559(2006)
Shaohua Fang, Li Yang*, *etal, Electrochemistry Communications,* 9,2696-2702(2007)
Zhang Huanqi, Yang Li*, *etal*, *Chinese Science Bulletin* 54(8),1322-1327(2009)
A. Orita, Li Yang*, *etal Journal of Power Sources* 195,6970-6976 (2010)

Physical and electrochemical properties of some Asymmetric Sulfonium ILs

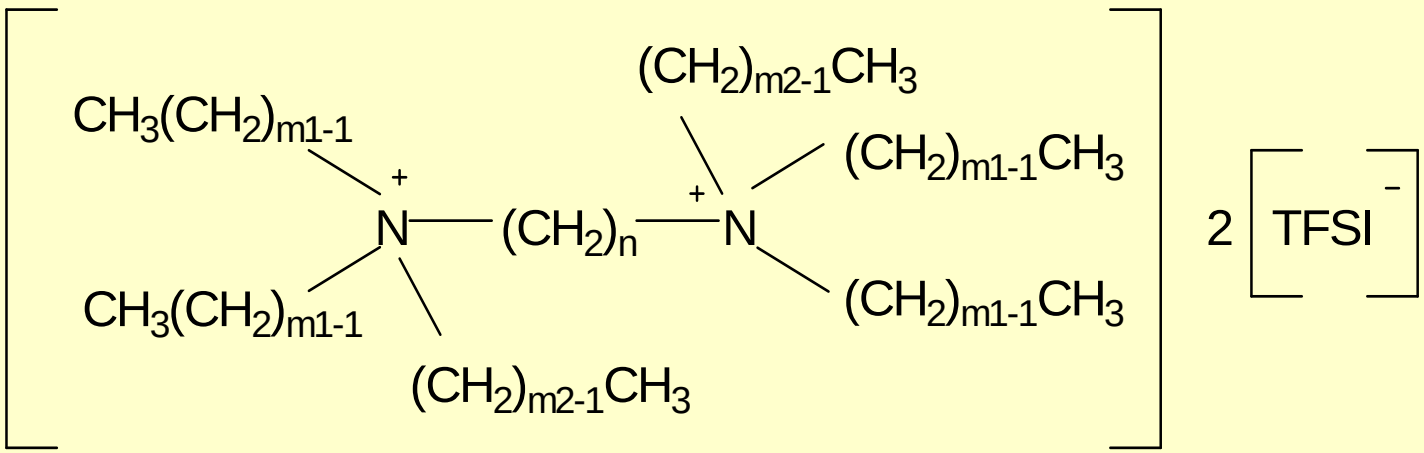
ILs	Melting Point / °C	Viscosity at 25°C /mPa s	Conductivity at 25°C /mS cm^{-1}	Decomposition temperature / °C	Electrochemical windows at 25°C / V
S_{113}TFSI	<-60	48	3.55	312.3	3.8
S_{115}TFSI	<-60	78	1.78	306.7	4.0
S_{221}TFSI	-22.6	36	5.80	303.4	3.9
S_{223}TFSI	-23.2	33	5.03	296.4	4.1
S_{224}TFSI	-28.9	42	3.07	296.7	3.7
S_{225}TFSI	<-60	43	2.86	295.5	3.8
S_{123}TFSI	<-60	39	4.70	306.7	4.0
S_{124}TFSI	<-60	50	3.35	311.6	3.2
S_{125}TFSI	<-60	57	2.50	309.1	3.7

Charge-discharge curves of the $Li/LiMn_2O_4$ cell



Test Condition: 2.5-4.2V, 0.1C rate

Structure of Dicationic Ionic Liquids



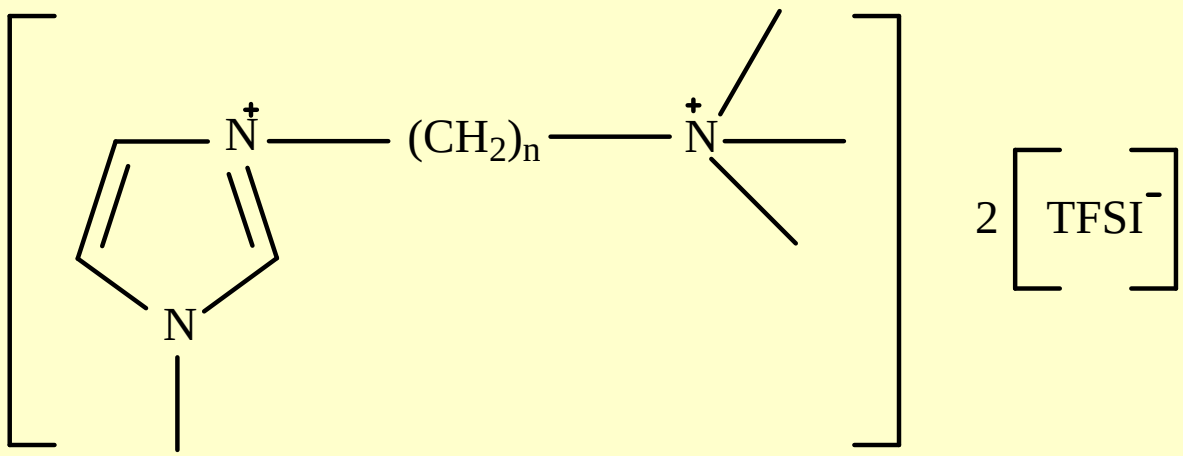
n = 2, 3, 6; m1 = 1, m2 = 2 ~ 8, $C_n(N_{11m2})_2$ - $TFSI_2$ Compounds 1-15

n = 9, 12; m1 = m2 =2, $C_n(N_{222})_2$ - $TFSI_2$ Compounds 16-17

n, spacer length; m = 2(2m1+m2), head group overall length

Zhengxi Zhang, Li Yang*, *etal, Journal of Power Sources,167, 217-222, (2007)*

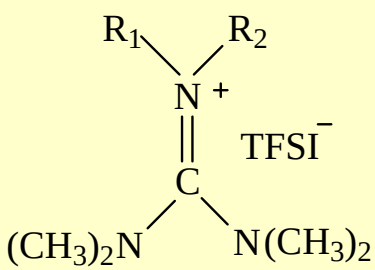
Structure of asymmetrical dicationic ILs

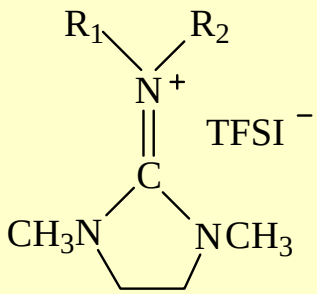


spacer length (n) = 2, 5, **MIC_nN_{111}-$TFSI_2$**, compounds 1-2

Zhengxi Zhang, Li Yang*, *etal* , *Electrochimica Acta 53, 4833-4838, (2008)*

Structures of guanidinium ionic liquids





Abbrevation

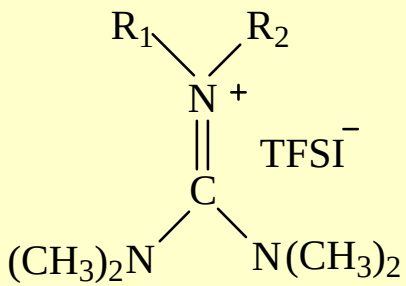
1g11TFSI	$R_1=R_2=CH_3$
1g12TFSI	$R_1=CH_3$, $R_2=C_2H_5$
1g13TFSI	$R_1=CH_3$, $R_2=n\text{-}C_3H_7$
1g14TFSI	$R_1=CH_3$, $R_2=n\text{-}C_4H_9$
1g22TFSI	$R_1=R_2=C_2H_5$
1g23TFSI	$R_1=C_2H_5$, $R_2=n\text{-}C_3H_7$
1g24TFSI	$R_1=C_2H_5$, $R_2=n\text{-}C_4H_9$
1g33TFSI	$R_1=R_2=n\text{-}C_3H_7$
1g34TFSI	$R_1=n\text{-}C_3H_7$, $R_2=n\text{-}C_4H_9$
1g44TFSI	$R_1=R_2=n\text{-}C_4H_9$

Abbrevation

cg11TFSI	$R_1=R_2=CH_3$
cg12TFSI	$R_1=CH_3$, $R_2=C_2H_5$
cg13TFSI	$R_1=CH_3$, $R_2=n\text{-}C_3H_7$
cg22TFSI	$R_1=R_2=C_2H_5$
cg23TFSI	$R_1=C_2H_5$, $R_2=n\text{-}C_3H_7$
cg33TFSI	$R_1=R_2=n\text{-}C_3H_7$

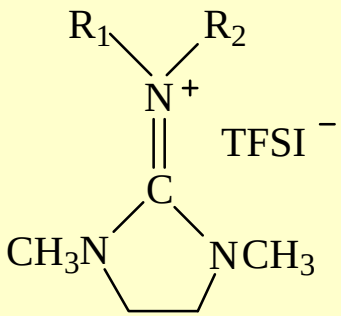
Shaohua Fang, Li Yang*, *etal, Electrochimica Acta, 54, 1752-1756, (2009)*

Structures of Functionalized Guanidinium ILs



Abbrevation

1g1(2o1)TFSI	$R_1=CH_3$, $R_2=CH_2CH_2OCH_3$
1g2(2o1)TFSI	$R_1=CH_2CH_3$, $R_2=CH_2CH_2OCH_3$
1g1ETFSI	$R_1=CH_3$, $R_2=CH_2COOCH_3$
1g2ETFSI	$R_1=CH_2CH_3$, $R_2=CH_2COOCH_3$



Abbrevation

cg1(2o1)TFSI	$R_1=CH_3$, $R_2=CH_2CH_2OCH_3$
cg2(2o1)TFSI	$R_1=CH_2CH_3$, $R_2=CH_2CH_2OCH_3$
cg1ETFSI	$R_1=CH_3$, $R_2=CH_2COOCH_3$
cg2ETFSI	$R_1=CH_2CH_3$, $R_2=CH_2COOCH_3$

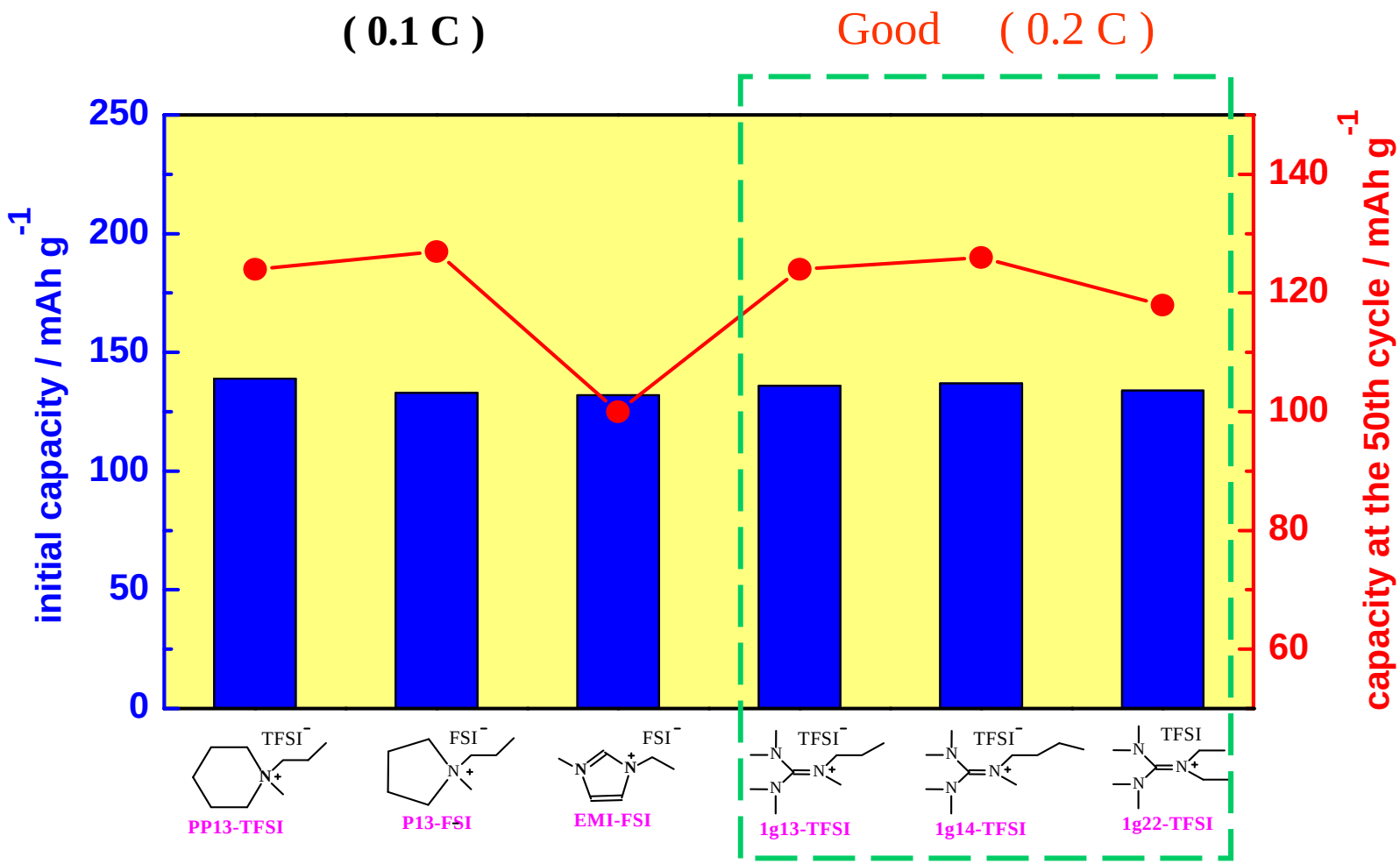
Shaohua Fang, Li Yang*, *etal, Electrochimica Acta,* 54,4269-4273(2009)

Fundamental Properties of these ILs

ILs	T_m / °C	η /mPa s	σ /mS cm^{-1}	T_d / °C	Electrochemical window V vs. Ag/Ag^+
1g1(2o1)TFSI	<-60	58	2.15	425.4	4.1 (-2.1 ~ +2.0)
1g2(2o1)TFSI	<-60	58	2.09	419.6	3.9 (-1.9 ~ +2.0)
cg1(2o1)TFSI	<-60	46	2.84	408.5	3.1 (-1.3 ~ +1.8)
cg2(2o1)TFSI	<-60	48	2.48	386.5	3.6 (-2.0 ~ +1.6)
1g1ETFSI	<-60	325	0.51	320.1	4.4 (-2.1 ~ +2.3)
1g2ETFSI	<-60	249	0.60	301.0	3.9 (-1.8 ~ +2.1)
cg1ETFSI	<-60	300	0.61	341.2	3.7 (-2.1 ~ +1.6)
cg2ETFSI	<-60	235	0.65	338.1	3.8 (-1.8 ~ +2.0)

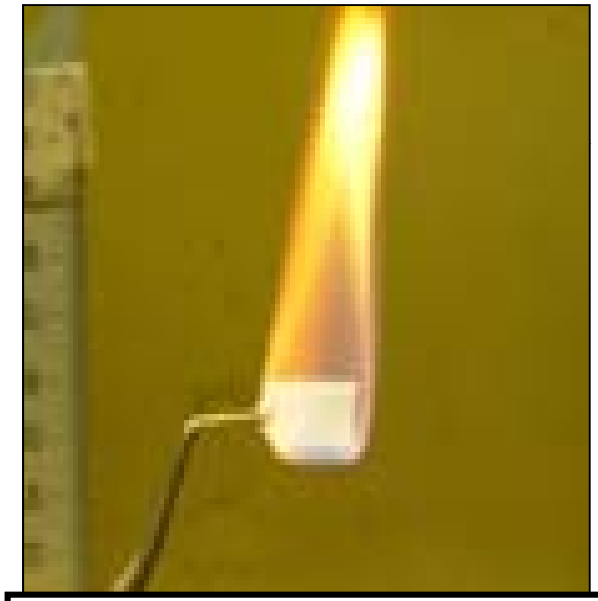
Comparing the performances of Li ion batteries using representative IL electrolytes

Lithium ion battery: $Li/LiCoO_2$



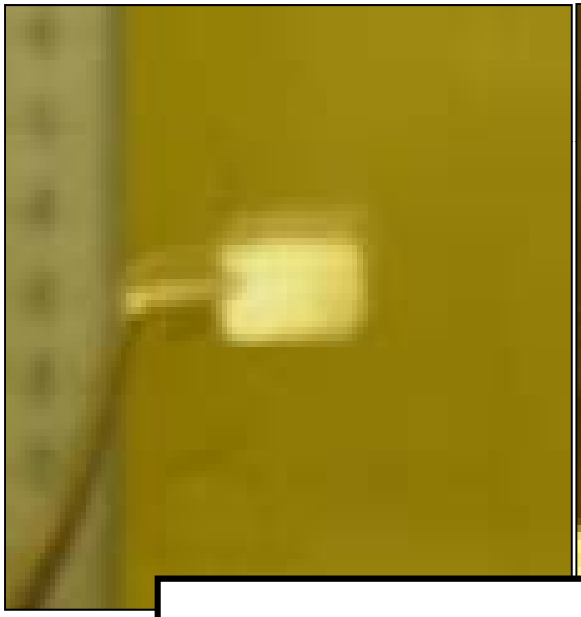
Flammability test

EC/DEC/DMC

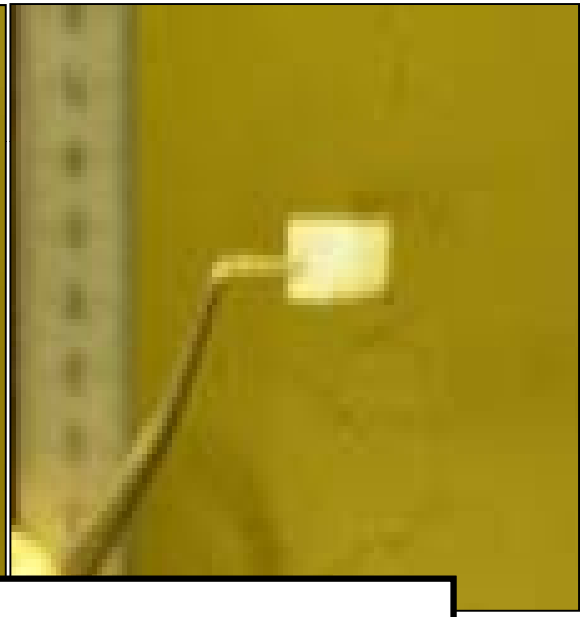


continued to burn

Guanidinium TFSI



Sulfonium TFSI



showed nonflammables

Conclusions of part I

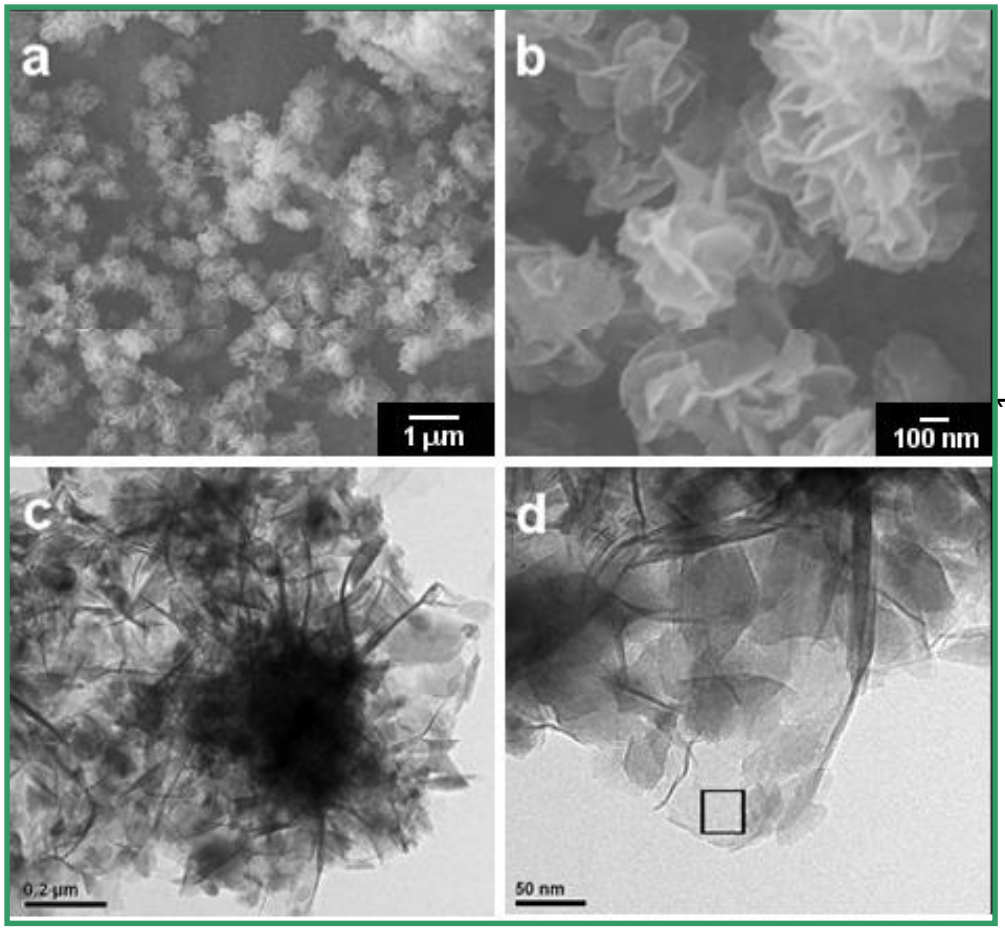
- Several new series of ionic liquid have been developed. They are promising new materials as safety liquid electrolytes in lithium ion battery;.
- The information on the structure-property relations of ionic liquid is still not sufficient.
- It is important to research on compatibility among the IL electrolytes and other parts of the battery.

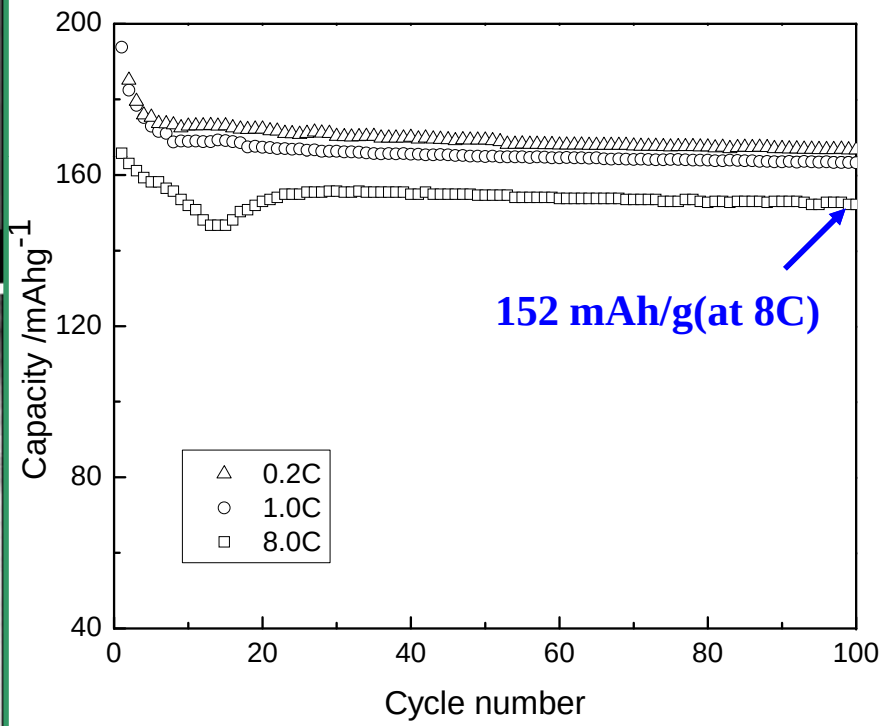
2 $Li_4Ti_5O_{12}$ anode materials

Nano/micro hierarchical $Li_4Ti_5O_{12}$ synthesized in our lab

- Flower-like microspheres assembled by $Li_4Ti_5O_{12}$ nanosheets
- Hollow microspheres assembled by $Li_4Ti_5O_{12}$ nanosheets
- Mesoporous $Li_4Ti_5O_{12}$ microspheres
- Hollow microspheres assembled by $Li_4Ti_5O_{12}$ nanotubes
- Microspheres assembled by sawtooth-like $Li_4Ti_5O_{12}$ nanosheets

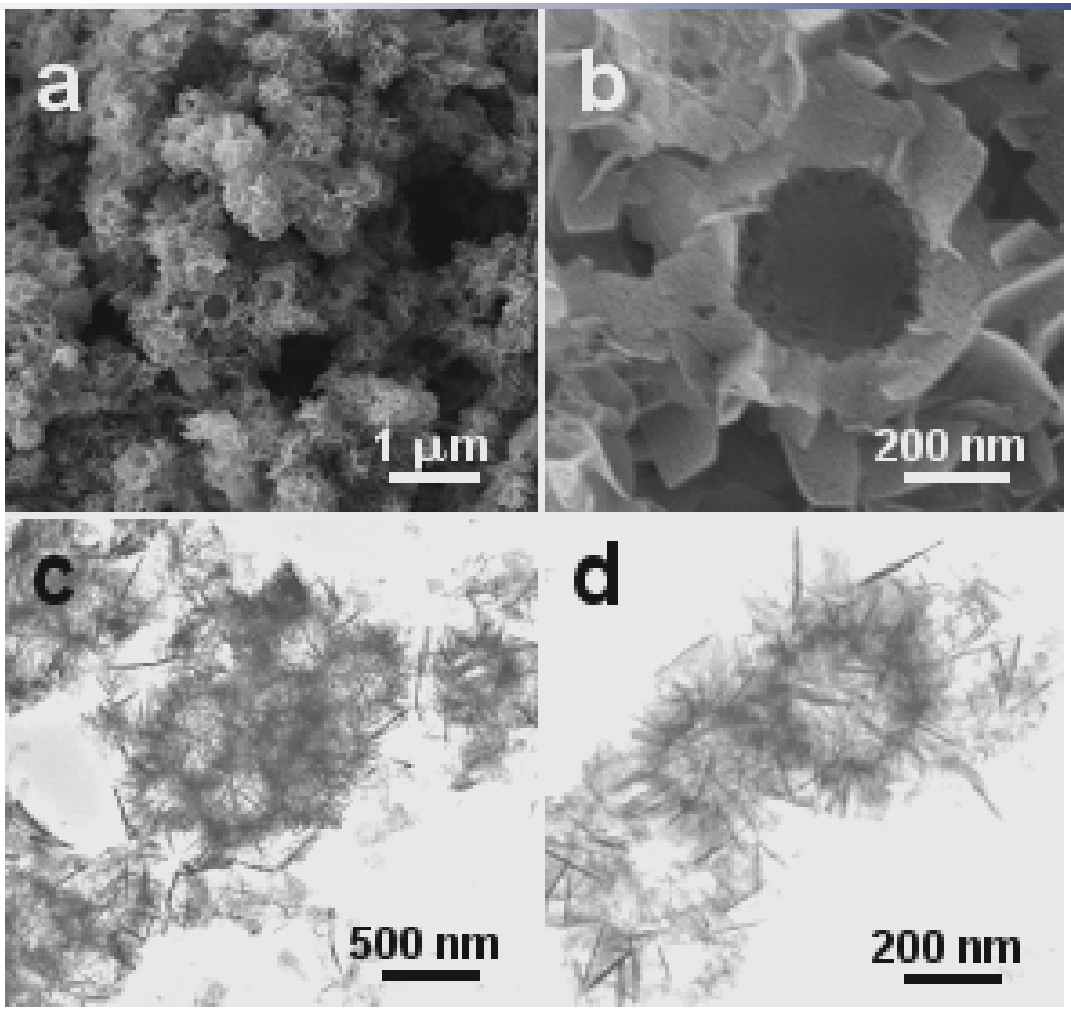
Flower-like $Li_4Ti_5O_{12}$ consisting of nanosheets





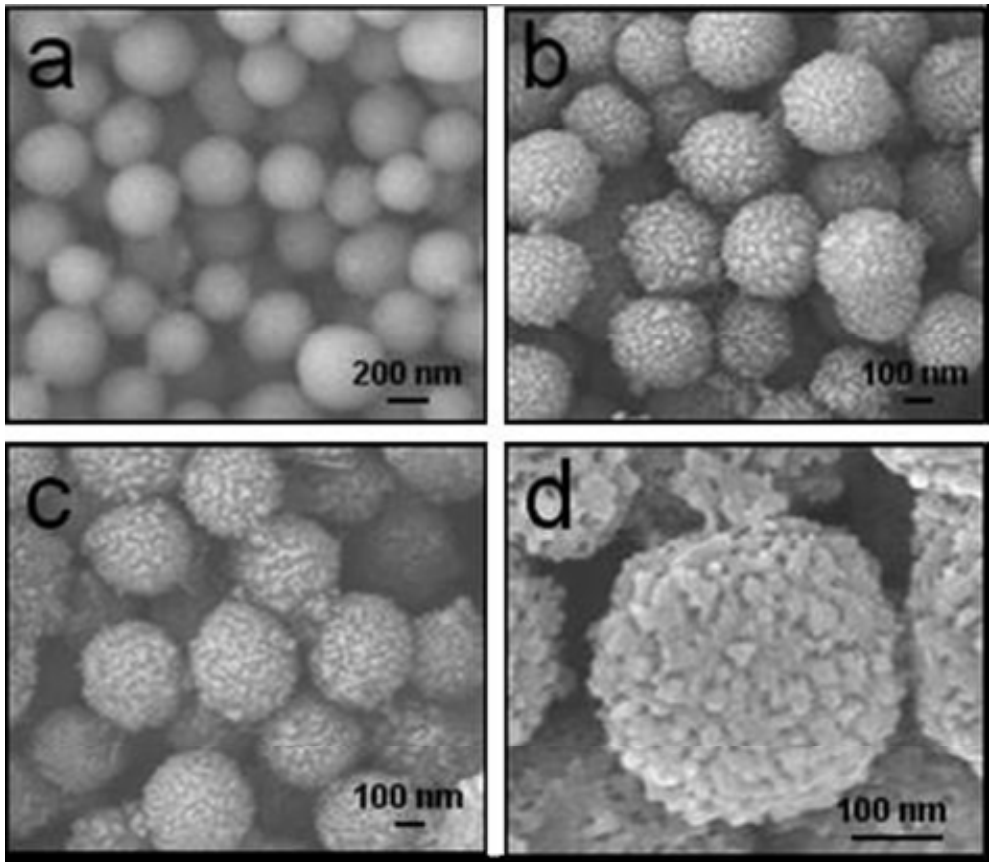
Y. Tang, L. Yang*, *et.al.*, *Electrochem. Commun.* 2008, 10, 1513–1516

Morphology of Nanosheet-based hollow microsphere



Y. Feng, L.Yang*, *et.al*., *Electrochim. Acta* 2009, 54, 6244-6249

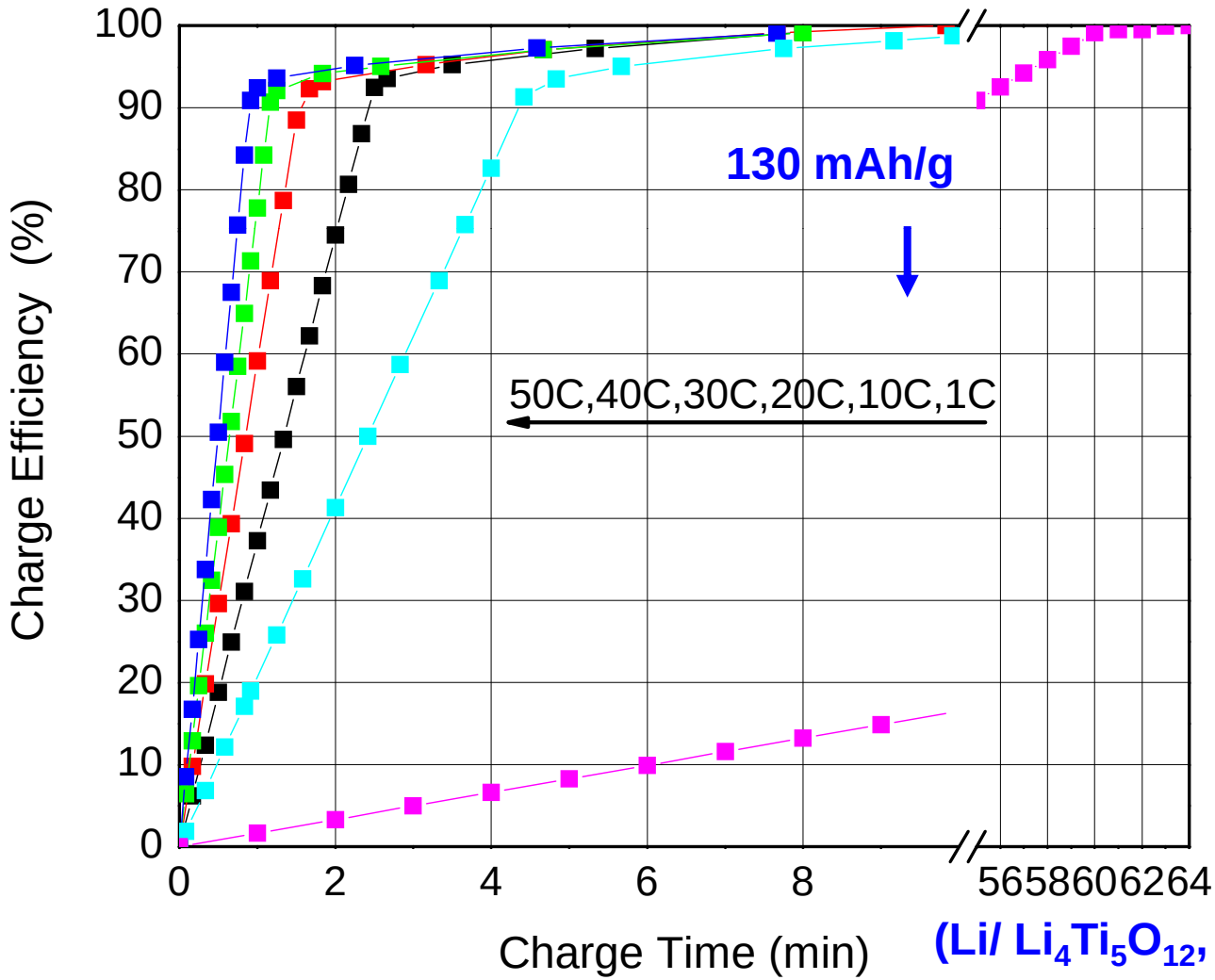
Morphology of mesoporous $Li_4Ti_5O_{12}$



$TiO_2 \cdot nH_2O$ (a), as-synthesized $Li_4Ti_5O_{12}$ spheres before annealing (b) and after annealing at 500 ^oC for 1h (c, d)

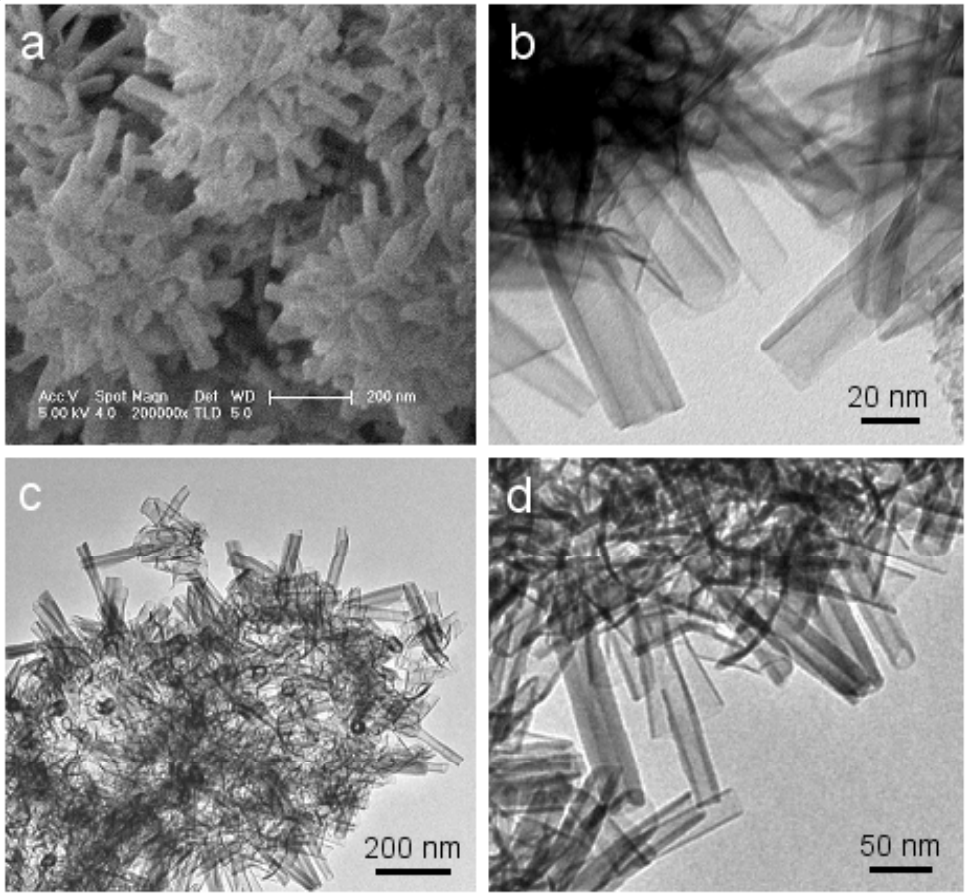
Y. Feng, L. Yang*, *et.al.*, *J. Mater. Chem.*, 2009, 19, 5980-5984

High rate feature of hollow $Li_4Ti_5O_{12}$



(Li/ $Li_4Ti_5O_{12}$, 1M $LiPF_6$)

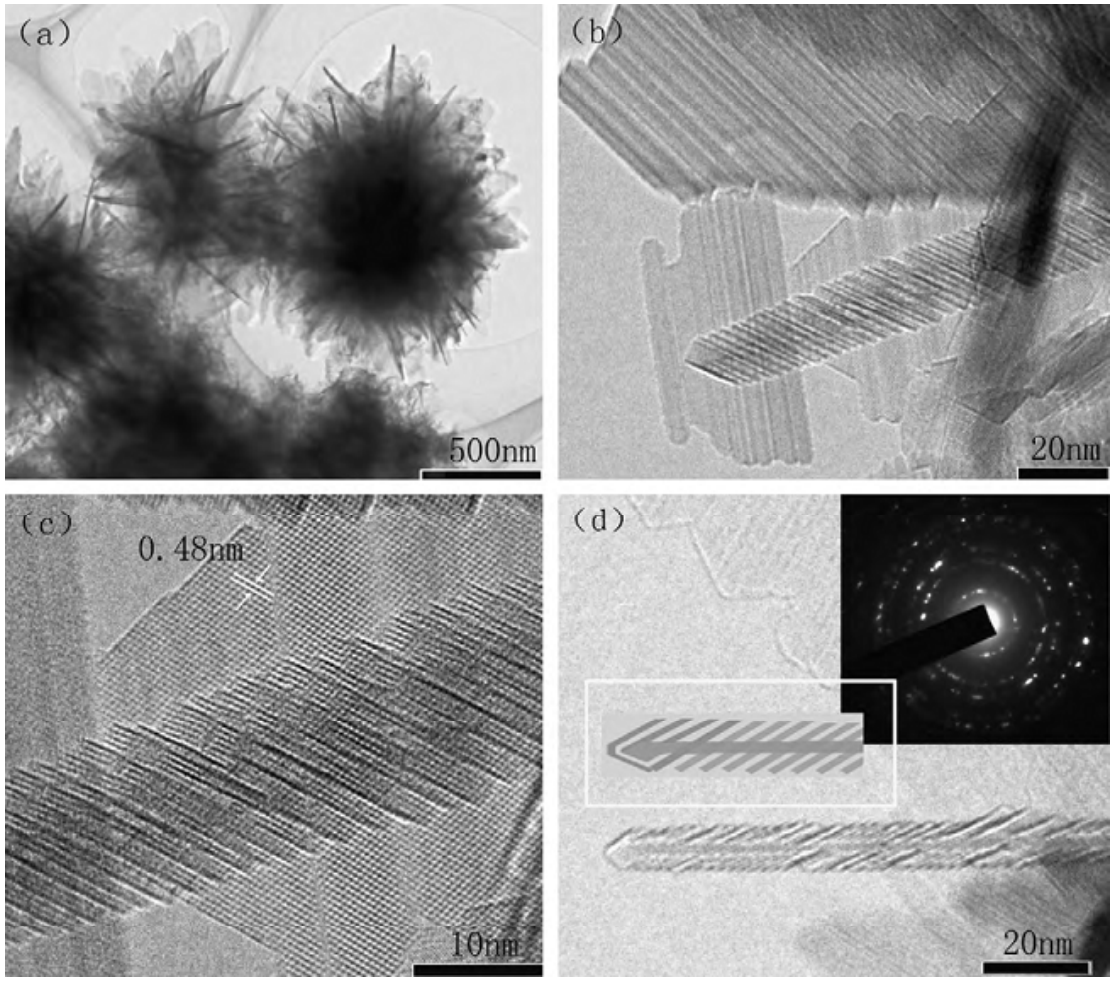
Morphology of nanotube-based hollow microspheres



Samples from 120 ^{o}C hydrothermal reaction before (a, b) and after calcination at 400 ^{o}C(c, d)

Yufeng Tang, Li Yang*, *etal*, *Langmuir* (in press)

$Li_4Ti_5O_{12}$ microspheres assembled by sawtooth-like nanosheets



J. Chen, L. Yang∗, *et al.* *Electrochimica Acta* 55 (2010) 6596–6600

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Thank you

for your attention!