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Supporting Information

Facile synthesis of manganese carbonate quantum dots/$Ni(HCO_3)_2$-$MnCO_3$ composites as advanced cathode materials for high energy density asymmetric supercapacitors

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Keywords: core-shell structure; nickel foam; graphene; binder-free; asymmetric supercapacitors

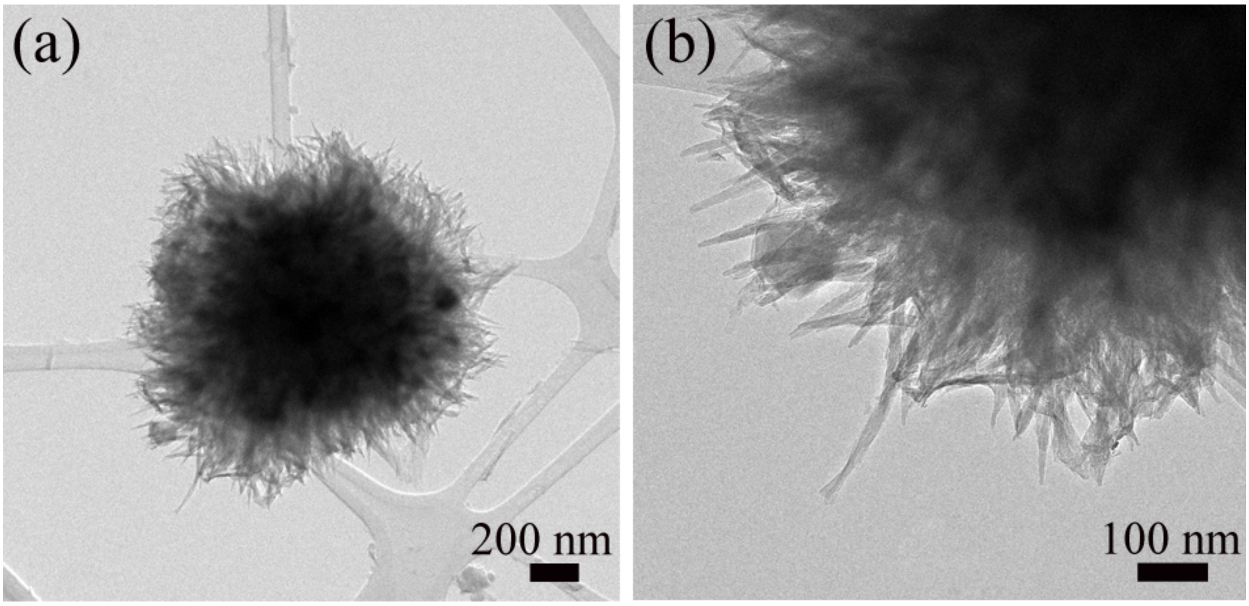


Fig. S1 Low magnification TEM images of the $MnCO_3$ QDs/NiH-Mn-CO_3 shell@needle composite structure.

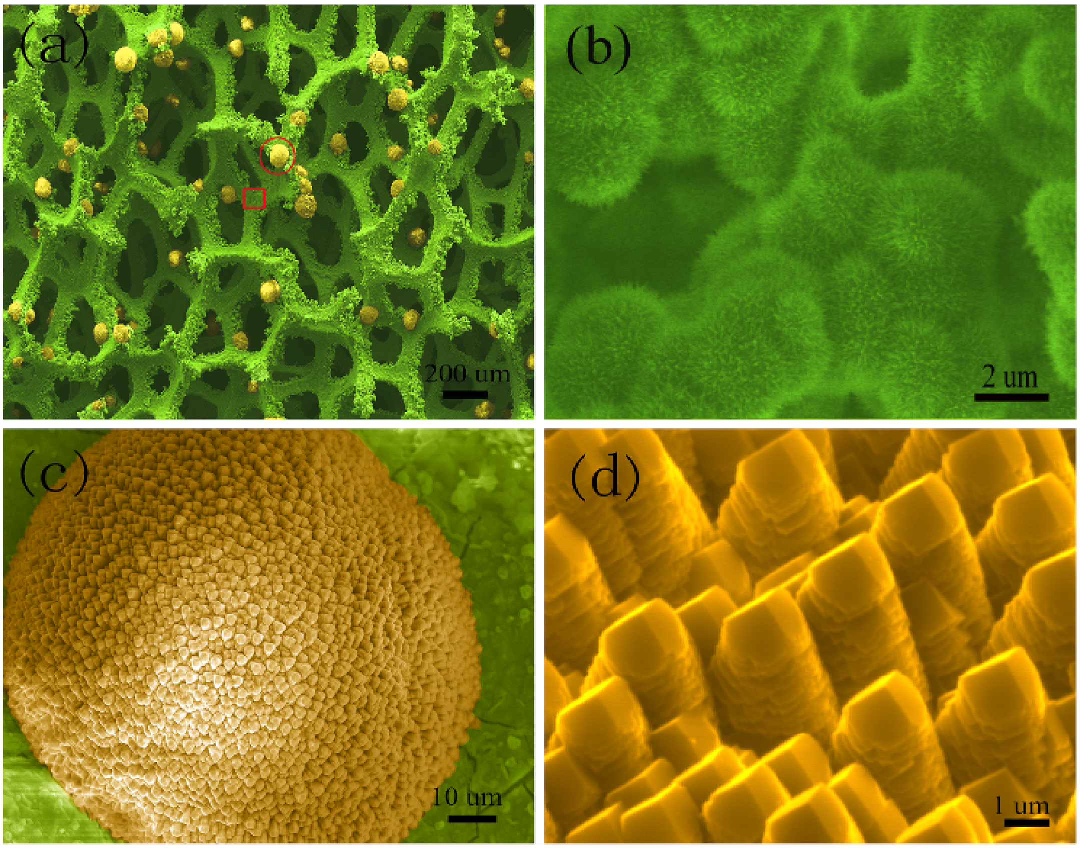
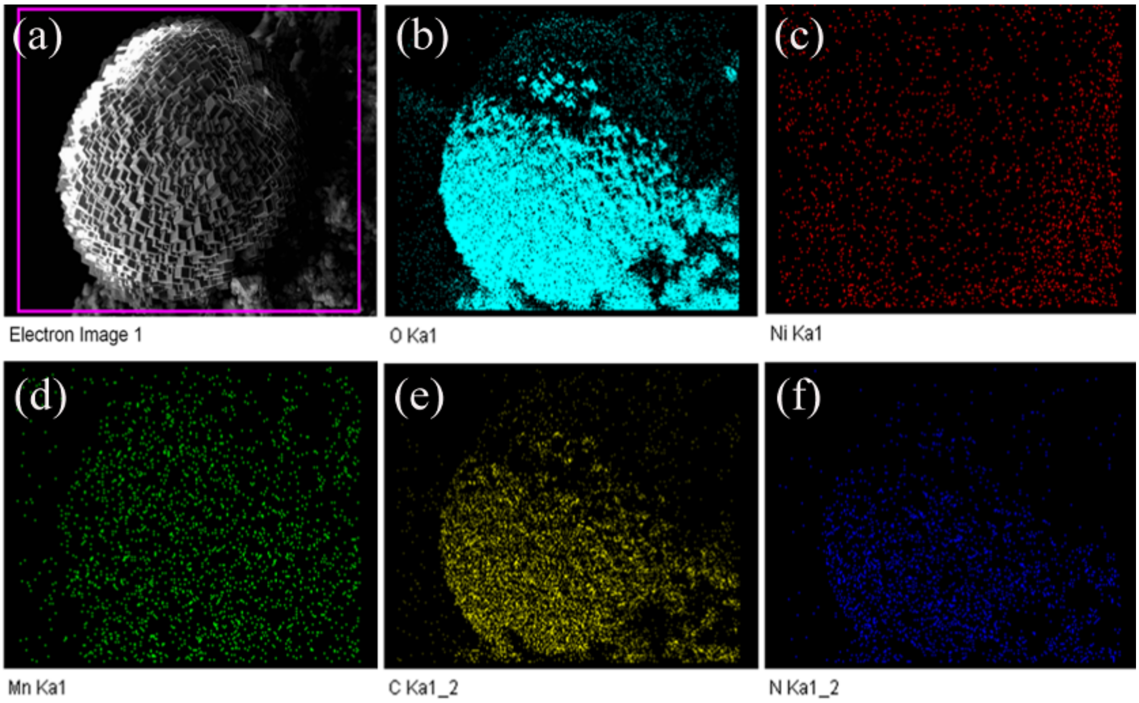
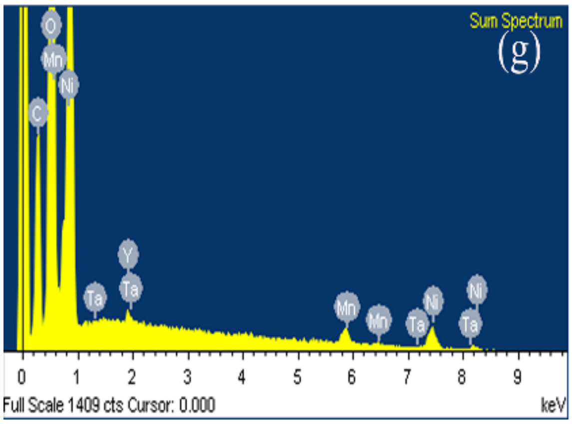


Fig. S2 SEM images of the (a) as-obtained porous $MnCO_3$ QDs/NiH-Mn-CO_3 composites grown on Ni foam at low magnification, (b) hedgehog-like nanoneedle at high magnification (red box area in a), (c) jackfruit-like ball (red ellipse area in a), and (d) surface morphology of the jackfruit-like ball at high magnification.





(h)

Element	Weight%	Atomic%
C K	17.79	23.46
O K	75.57	74.79
Mn K	1.58	0.45
Ni K	4.37	1.18
Y L	0.64	0.11
Ta M	0.06	0.01
Totals	100.00	

Fig. S3 (a) SEM images of the jackfruit-like ball with corresponding elemental mapping images of O (b), Ni (c), Mn (d), C (e), and N (f); (g) Selected-area EDX spectrum of the jackfruit-like ball in (a), and (h) corresponding elements content.

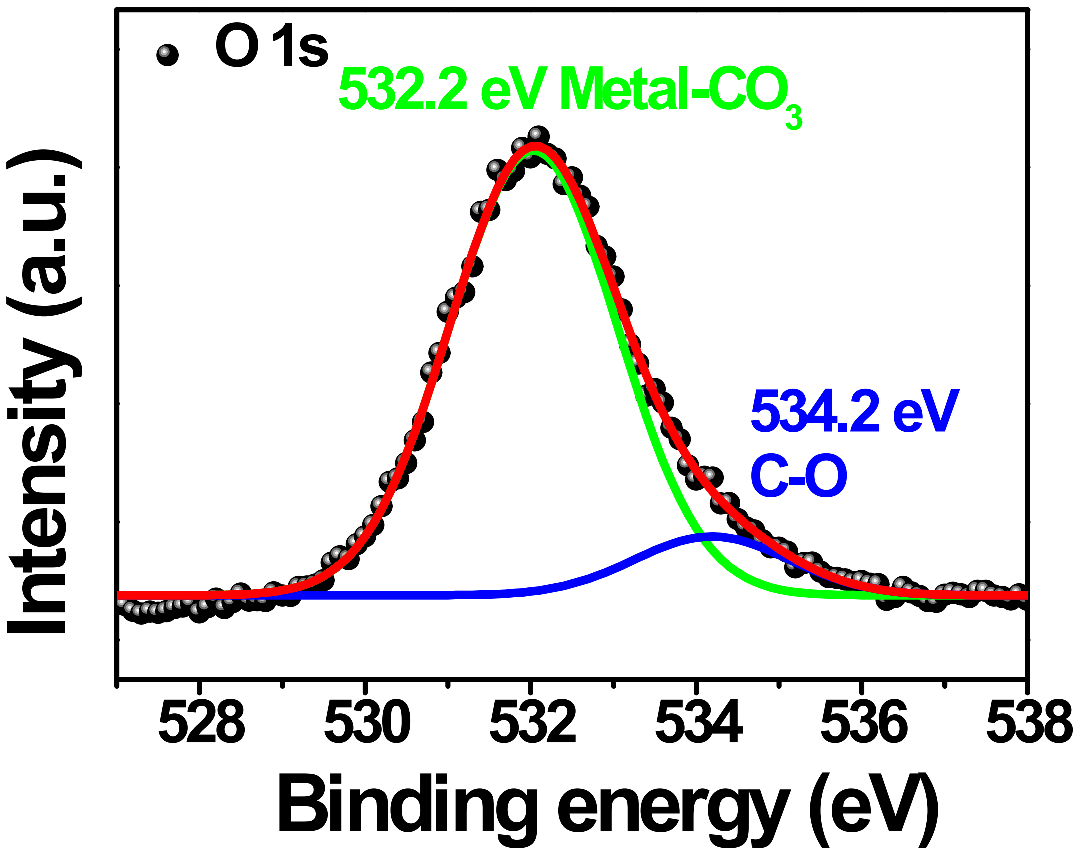


Fig. S4 O 1s XPS spectra of $MnCO_3$ QDs/NiH-Mn-CO_3 composites.

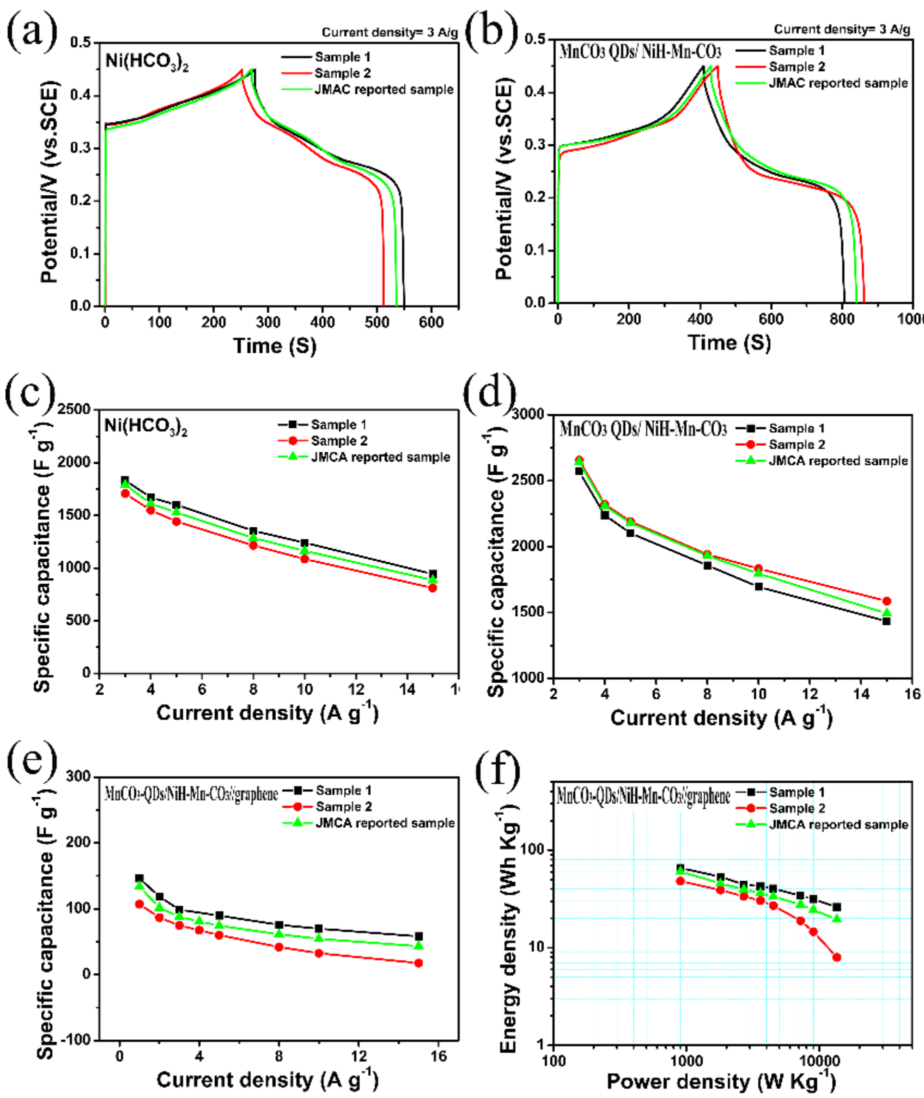


Fig. S5 Electrochemical performance of three different batches of the $Ni(HCO_3)_2$ and $MnCO_3$ QDs/NiH-Mn-CO_3 composite samples before cycling tests. Galvanostatic charge-discharge curves of (a) $Ni(HCO_3)_2$ and (b) $MnCO_3$ QDs/NiH-Mn-CO_3 composite electrode. (c) The specific capacitances of $Ni(HCO_3)_2$ electrodes at different current densities. (d) The specific capacitances of $MnCO_3$ QDs/NiH-Mn-CO_3 composite electrodes at different current densities. (e) The specific capacitances of $MnCO_3$ QDs/NiH-Mn-CO_3//Graphene asymmetric supercapacitors at different current densities. (e) The energy densities of $MnCO_3$ QDs/Ni-Mn-CO_3//Graphene asymmetric supercapacitors and the corresponding power densities.

Table S1. Comparison of maximum *Cs*, energy and power densities of the reported nickel/manganese oxide/hydroxide based composite pseudocapacitive materials and the present work.

/ Positive electrodes /	C_s (F g^{-1})	Energy density [Wh/kg^{-1}]	Power density [W/kg^{-1}]	Electrolyte	Ref.
$MnNi(OH)_2$ LDH nanoparticles	160 (1 mA cm^{-2})			1 M Na_2SO_4	*[1]*
Porous plate $NiMn_2O_4$	180 (250 mA/g)				*[2]*
Ni-doping Mn_3O_4	184 (0.5 A/g)			1 M Na_2SO_4	*[3]*
$Ni(OH)_2/MnO_2$ core shell	355 (0.5 A/g)	41.2	500	1 M Na_2SO_4	*[4]*
$Ni_{0.2}Mn_{0.8}O_x$	380 (5 mVs^{-1})			0.5 M Na_2SO_4	*[5]*
Ni-Mn Oxide films	424 (20 mVs^{-1})			0.5 M Na_2SO_4	*[6]*
NiO/MnO_2 core shell	528.0 (1 mVs^{-1})			1 M LiOH	*[7]*
MnO_2/NiO	681 (1A/g)		43000	0.5 M KOH	*[8]*
Sponge-like $NiCo_2O_4/MnO_2$	935 (1 A/g)	46.75	300	1 M KOH	*[9]*
Ni-Mn Oxide	1016 (0.5A/g)			6 M KOH	*[10]*
3D NiO@MnOOH	1890.5 (1.7A/g)	80.0		1 M LiOH	*[7]*
Porous $Ni(OH)_2$-MnO_2-RGO	1985 (2A/g)	54.0	392	1 M KOH	*[11]*
NiMn-LDH/CNT	2960 (1.5A/g)				*[12]*
Ni-Mn sulfide	1430 (0.5A/g)			6 M KOH	*[10]*
Spinel Mn-Ni-Co ternary Oxide	638 (1A/g)	79.8	250	6 M KOH	*[13]*
Graphene/NiO-MnO_2	242 (0.2 mVs^{-1})			6 M KOH	*[14]*
$Ni_{1/3}Co_{1/3}Mn_{1/3}(OH)_2$	1402 (1.0 mVs^{-1})				*[15]*
NiO-MnO_2/MWCNT	193.5 (5 mVs^{-1})			6 M KOH	*[16]*
Ni-Mn/ordered carbon	434 (5 mVs^{-1})			2 M KOH	*[17]*
Mn-Ni-Co Oxide composite	1260 (5 mA)			6 M KOH	*[18]*
NiO microspheres	619 (5 mA cm^{-2})			6 M KOH	*[19]*
Nanospherical porous NiO	1201 (0.5A/g)			2 M KOH	*[20]*
NiO-3D graphene	1829 (3 A/g)			1 M NaOH	*[21]*
NiO/MWCNTs	1727 (5 mA cm^{-2})			2 M KOH	*[22]*
Mn_3O_4 nanorods	263 (1 A/g)			4 M NaOH	*[23]*
MnO_2 nanowires	237 (2 mVs^{-1})			0.5 M Na_2SO_4	*[24]*
MnO_2 petal nanosheet/graphene	516.8 (1 mVs^{-1})			1 M Na_2SO_4	*[25]*

GO/ Mn_3O_4	344 (5 mVs^{-1})			1 M Na_2SO_4	*[26]*
$MnCO_3$ QDs/NiH-Mn-CO_3	2622.9 (3A g^{-1})	73.8	675	1 M KOH	This work

Table S2. Comparison of the maximum energy densities and power densities and voltage range of the reported nickel or manganese oxide/hydroxide based asymmetric supercapacitors with those of the present work.

/ Positive electrodes//Negative electrodes /	Energy density [$Wh\cdot kg^{-1}$]	Power density [$W\cdot kg^{-1}$]	Voltage range	Ref.
NiO particles//AC	19.0	120	0.8-1.5 V	[27]
$Ni(OH)_2$//AC	25		0.6-1.3 V	[28]
$Ni(OH)_2$//graphene	30	1000	0-1.6 V	[29]
NiO/graphene//N-CNT	32	700	0-1.4 V	[30]
CNT/$Ni(OH)_2$//rGO	35.24	1807	0-1.8 V	[31]
α-$Ni(OH)_2$//AC	42.3	110	0.4-1.6 V	[32]
3D graphene/$Ni(OH)_2$//AC	52.7	444.4	0-1.6 V	[33]
$Ni(OH)_2$/graphene//porous graphene	77.8	174.7	0-1.6 V	[34]
NiO/graphene//activated carbon	138	5250	0-1.5 V	[21]
MnO_2//AC	10	3600	0-2.2 V	[35]
Mn_3O_4/RGO//N-doped GS	11.11	23500	0-2 V	[36]
Graphene/MnO_2//CNT textiles	12.5		0-1.5 V	[37]
Activation of Mn_3O_4//graphene	20.1	2000	0-2 V	[38]
RGO/MnO_2/CNT//AC	27	130	0-2 V	[39]
MnO_2 Nanorods//AC	28.4	150	0-1.8 V	[40]
MnO_2 nanowire/graphene //graphene	30.4	100	0-2 V	[41]
Mn_3O_4@GR//AC	34.6	500	0-1.6 V	[42]
$LiMn_2O_4$//AC	35	100	0.5-1.8 V	[43]
Polyaniline/$Li(Mn_{1/3}Ni_{1/3}Fe_{1/3})O_2$//AC	49	1000	0-3 V	[44]
$LiNi_{0.5}Mn_{1.5}O_4$//AC	56		1-3 V	[45]
$MnCO_3$ QDs/NiH-Mn-CO_3//graphene	58.1	900	0-1.8 V	This work

References

1. S. Anandan, C. Y. Chen, J. J. Wu, RSC Advances 2014, **4**, 55519.
2. H. Pang, J. W. Deng, S. M. Wang, S. J. Li, J. M. Du, J. Chen, J. S. Zhang, RSC Advances 2012, **2**, 5930.
3. R. Dong, Q. Ye, L. Kuang, X. Lu, Y. Zhang, X. Zhang, G. Tan, Y. Wen, F. Wang, ACS applied materials & interfaces 2013, **5**, 9508.
4. H. Jiang, C. Li, T. Sun, J. Ma, Chemical Communications 2012, 48, 2606.
5. P. Ahuja, S. K. Ujjain, R. K. Sharma, G. Singh, RSC Advances 2014, **4**, 57192.
6. H.-M. Lee, K. Lee, C.-K. Kim, Materials 2014, **7**, 265.
7. J. Sun, W. Li, B. Zhang, G. Li, L. Jiang, Z. Chen, R. Zou, J. Hu, Nano Energy 2014, **4**, 56.
8. Rusi, S. R. Majid, Electrochimica Acta 2014, **138**, 1.
9. G. Li, W. Li, K. Xu, R. Zou, Z. Chen, J. Hu, Journal of Materials Chemistry A 2014, **2**, 7738.
10. H. Wan, J. Jiang, Y. Ruan, J. Yu, L. Zhang, H. Chen, L. Miao, S. Bie, Particle & Particle Systems Characterization 2014, **31**, 857.
11. H. Chen, S. Zhou, L. Wu, ACS Appl Mater Interfaces 2014, **6**, 8621.
12. J. Zhao, J. Chen, S. Xu, M. Shao, Q. Zhang, F. Wei, J. Ma, M. Wei, D. G. Evans, X. Duan, Advanced Functional Materials 2014, **24**, 2938.
13. L. Li, Y. Zhang, F. Shi, Y. Zhang, J. Zhang, C. Gu, X. Wang, J. Tu, ACS applied materials & interfaces 2014, **6**, 18040.
14. S. G. Hwang, J. E. Hong, G. O. Kim, H. M. Jeong, K. S. Ryu, ECS Solid State Letters 2012, **2**, M8.
15. G. Wang, L. Liu, L. Zhang, J. Zhang, Ionics 2013, **19**, 689.
16. S.-G. Hwang, S.-H. Ryu, S.-R. Yun, J. M. Ko, K. M. Kim, K.-S. Ryu, Materials Chemistry and Physics 2011, **130**, 507.
17. J. Feng, B. Tang, J. Zhao, P. Liu, J. Xu, Journal of Applied Electrochemistry 2011, **41**, 901.
18. J.-M. Luo, B. Gao, X.-G. Zhang, Mater Res Bull 2008, **43**, 1119.
19. M. Q. Fan, B. Ren, L. Yu, Q. Liu, J. Wang, D. L. Song, J. Y. Liu, X. Y. Jing, L. H. Liu, Crystengcomm 2014, **16**, 10389.
20. Y. Wang, B. Chang, D. Guan, K. Pei, Z. Chen, M. Yang, X. Dong, Materials Letters 2014, **135**, 172.
21. C. Wang, J. Xu, M.-F. Yuen, J. Zhang, Y. Li, X. Chen, W. Zhang, Advanced Functional Materials 2014, **24**, 6372.
22. G. S. Gund, D. P. Dubal, S. S. Shinde, C. D. Lokhande, ACS Appl Mater Interfaces 2014, **6**, 3176.
23. D. W. Li, F. H. Meng, X. L. Yan, L. S. Yang, H. Heng, Y. Zhu, Nanoscale Res Lett 2013, **8,** 535.
24. T. Yousefi, A. N. Golikand, M. H. Mashhadizadeh, M. Aghazadeh, Current Applied Physics 2012, **12**, 193.

25. X. Feng, Z. Yan, N. Chen, Y. Zhang, Y. Ma, X. Liu, Q. Fan, L. Wang, W. Huang, Journal of Materials Chemistry A 2013, **1**, 12818.
26. G. S. Gund, D. P. Dubal, B. H. Patil, S. S. Shinde, C. D. Lokhande, Electrochimica Acta 2013, **92**, 205.
27. H. Inoue, Y. Namba, E. Higuchi, Journal of Power Sources 2010, **195**, 6239.
28. J. H. Park, O. O. Park, K. H. Shin, C. S. Jin, J. H. Kim, Electrochemical and Solid-State Letters 2002, **5**, H7.
29. C.-C. Hu, J.-C. Chen, K.-H. Chang, J Power Sources 2013, **221**, 128.
30. H. Wang, H. Yi, X. Chen, X. Wang, Journal of Materials Chemistry A 2014, **2**, 3223.
31. R. R. Salunkhe, J. Lin, V. Malgras, S. X. Dou, J. H. Kim, Y. Yamauchi, Nano Energy 2015, **11**, 211.
32. J.-W. Lang, L.-B. Kong, M. Liu, Y.-C. Luo, L. Kang, Journal of Solid State Electrochemistry 2009, **14**, 1533.
33. H. Yan, J. Bai, B. Wang, L. Yu, L. Zhao, J. Wang, Q. Liu, J. Liu, Z. Li, Electrochimica Acta 2015, **154**, 9.
34. J. Yan, Z. Fan, W. Sun, G. Ning, T. Wei, Q. Zhang, R. Zhang, L. Zhi, F. Wei, Advanced Functional Materials 2012, **22**, 2632.
35. T. Brousse, M. Toupin, D. Bélanger, Journal of The Electrochemical Society 2004, **151**, A614.
36. C.-L. Liu, K.-H. Chang, C.-C. Hu, W.-C. Wen, J Power Sources 2012, **217**, 184.
37. G. H. Yu, L. B. Hu, M. Vosgueritchian, H. L. Wang, X. Xie, J. R. McDonough, X. Cui, Y. Cui, Z. N. Bao, Nano Lett 2011, **11**, 2905.
38. T. H. Wu, Y. H. Chu, C.-C. Hu, L. J. Hardwick, Electrochemistry Communications 2013, **27**, 81.
39. Y. Cheng, H. Zhang, S. Lu, C. V. Varanasi, J. Liu, Nanoscale 2013, **5**, 1067.
40. Q. T. Qu, P. Zhang, B. Wang, Y. H. Chen, S. Tian, Y. P. Wu, R. Holze, J Phys Chem C 2009, **113**, 14020.
41. Z. S. Wu, W. C. Ren, D. W. Wang, F. Li, B. L. Liu, H. M. Cheng, ACS Nano 2010, **4**, 5835.
42. Y. Xiao, Y. Cao, Y. Gong, A. Zhang, J. Zhao, S. Fang, D. Jia, F. Li, J Power Sources 2014, **246**, 926.
43. Y.G. Wang, Y.Y. Xia, Journal of The Electrochemical Society 2006, **153**, A450.
44. K. Karthikeyan, S. Amaresh, V. Aravindan, H. Kim, K. S. Kang, Y. S. Lee, Journal of Materials Chemistry A 2013, **1**, 707.
45. H. Wu, C. V. Rao, B. Rambabu, Mater Chem Phys 2009, **116**, 532.