Int. J. Electrochem. Sci., 11 **(2016)** 6791 – 6798, doi: 10.20964/2016.08.44

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Short Communication

Synthesis of Novel CoS_2 Nanodendrites with High Performance Supercapacitors

Daojun Zhang[1], *Huaixin Liu*[2], *Jingchao Zhang*[1], *Xiao Wang*[1], *Renchun Zhang*[1], *Jingyang Zhou*[1], *Jing Zhong*[3,*], *Baiqing Yuan*[1,*]

[1] Henan Province Key Laboratory of New Optoelectronic Functional Materials, College of Chemistry and Chemical Engineering, Anyang Normal University, Anyang 455000, Henan, China
[2] College of Chemistry and Enviromental Engineering, Shanxi Datong University, Datong 037009, Shanxi, China
[3] School of Chemical Engineering, Taishan Medical University, Taian 271016, Shandong, China
[*]E-mail: baiqingyuan1981@126.com, jzhong2005@126.com

Received: 29 April 2016 / *Accepted:* 11 May 2016 / *Published:* 7 July 2016

Cobalt disulfide (CoS_2) nanodendrites were synthesized via a one-step solvothermal approach with high yield, the obtained nanoparticles present uniform size and 3D morphology assembled by nanosheets. The as-prepared CoS_2 nanodendrites deliver relatively high specific capacitance of 311.06 F g^{-1} at 1 A g^{-1} and good cycle stability, notably, CoS_2 nanodendrites exhibt excellent cycling durability after 3000 cycles with a total capacitance loss of about 19.78 % (80.22 %) at 4 A g^{-1}.

Keywords: Cobalt disulfide; Nanodendrites; Supercapacitors; Metal sulfides

1. INTRODUCTION

Nowdays, the dependece of fossil fuels cause serious envrionment pollution and rapid energy depletion, various high-capacitance electrochemical energy conversion and storage technologies are developed to deal with the growing necessary of mobile energy devices for renewable clean energy [1-12]. Supercapacitors, as an important class of useful energy storage apparatus, have some merits with high speed charge-discharge capability, high power density and excellent cycling durability [13-20].

As a new types of energy storage material, recently, transition metal sulfides are popularly studied due to their excellent electrochemical performance [21-28]. Among the various metal sulfides, cobalt sulfides have multivariate oxidation states for charge transfer, high electronic conduction, inexpensive and environmentally friendly, which were promised as good electrode materials in

supercapacitors and lithium ion batteries [29]. Cobalt sulfides comprise many different phases such as CoS, CoS_2, Co_3S_4, Co_9S_8, and $CoS_{1.097}$, and each cobalt sulfide owns its merits. Recent researches on micro/nanostructured cobalt disulfide (CoS_2) indicate that CoS_2 micro/nanostructures with different morphologies, such as ellipsoids [30], octahedrons [31], micro- and nanostructures [32], hierarchical mesoporous microspheres [33] and worm-like[34], hollow spheres [35, 36], nanocubes [37], and nanocomposites [38-41], can improve the electrochemical properties of CoS_2 electrodes for lithium-ion batteries and supercapacitors. So far, many methods including template [36], microwave [42], ion exchange reaction [43], solid-phase synthesis [44], solvothermal methods[45] have been devoted to the fabrication of different morphological nanostructured CoS_2. However, the synthesis of CoS_2 nanodendrites has not been well established.

On the basis of the above considerations, herein, we reported a facile solvothermal synthesis route of CoS_2 nanodendrites, and the possible application as supercapacitor electrode material of the nanodendrites was further surveyed. The as-prepared CoS_2 nanodendrites exhibited high capacitance and well cycle stability during a high speed charge and discharge process.The results indicate that the CoS_2 nanodendrite electrode shows great potential for supercapacitors application.

2. EXPERIMENTAL SECTION

2.1 Synthesis of CoS_2 nanodendrites

The synthesis process is as follow, the powder of $C_4H_6CoO_4{\cdot}4H_2O$ (0.0249 g, 0.1 mmol), polyvinyl prorolindone (PVP, K30, 100 mg) and trisodium citrate dihydrate (5.8 mg, 0.02 mmol) were carefully weight and dispersed in the mixture of Triton X-100 (1 mL), N,N-dimethylacetamide (4 mL), deionized water (5.5 mL) and a little of hexane (~0.5 mL). And then, 150 μL of cyclohexylamine was add to tune the pH of the solution. At last, a large amount of cysteine (0.0485 g, 0.4 mmol) was pour into the mixed solution when under high speed stirring. The mixture was further agitated for 20 minutes, sealed into the steel autoclave and heated the oven to 180 ^oC, and the reaction time is about 24 h. The black pwder were washed by absolute ethanol and deionized water and aquired by centrifugation, and finally dried at 80 ^oC for 1 h in vaccum.

2.2 Materials characterization

X-ray diffraction (XRD) patterns of CoS_2 nanodendrites were recorded on a Rigaku-Ultima III with Cu Ka radiation (λ=1.5418Å). The morphology and size of the sample was measurements by field-emission scanning electron microscopy (FSEM) on a Hitachi SU8010 instrument. The nanostructure was further studied by transmission electron microscopy (TEM) on a FEI Tecnai G2 s-twin D573. The specific surface areas of the samples were determined by N_2 adsorption on Gemini VII 2390 analyzer at 77 K by using the volumetric method.

2.3 The preparation and measurement of electrochemical supercapacitor electrode

The electrochemical tests including cyclic voltammetry (CV) and galvanostatic charge–discharge measurements were conducted on a CHI 760E electrochemical workstation. The standard three-electrode setup was consititued by a saturated calomel electrode, a rectangular platinum foil and a modified nickel foam, they are respectively used as the reference, counter and work electrodes. The working electrode was prepared by wetting grinding of CoS_2 powder, acetylene black, and polyvinylidene fluoride through adding N-methyl-2-pyrrolidone to obtain a high quality slurry. The dosage of them are 75%:15%:10%. Then the slurry was transfered to a nickel foam with the area of 1 cm^2, pressed and dried under a vacuum oven at 100°C for 10 h.

3. RESULTS AND DISCUSSION

3.1 Structure and morphology characterization

The as-prepared CoS_2 nanodendrites were firstly analyzed by XRD to investigate the crystallographic structure.

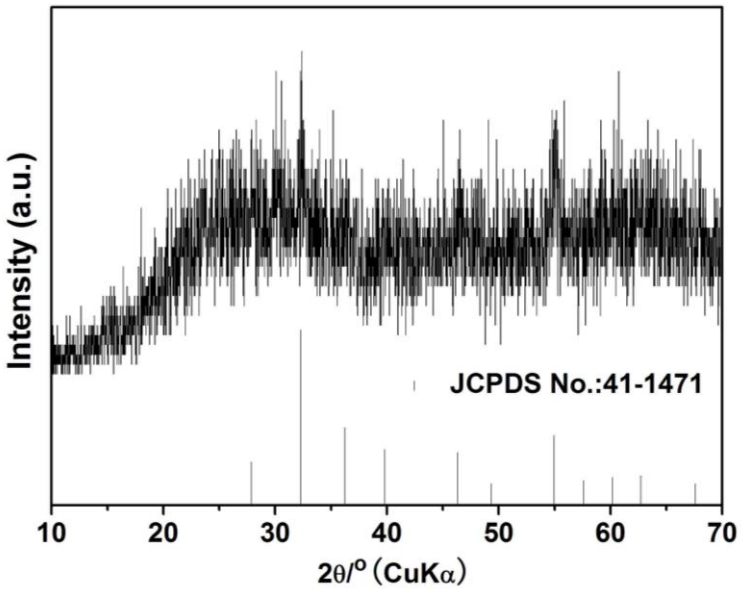

Figure 1. XRD patterns of CoS_2 nanodendrite. Vertical lines at the bottom represent the standard PDF card of α-CoS_2.

As shown in Fig.1, all the diffraction peaks can match with the standard crystallographic spectrum of CoS_2 (JCPDS 41-1471). Notably, no additional peaks are probed in the sample, which implied the high purity of the as-synthesized CoS_2 nanodendrite. As shown in Fig. 2, the analysis of N_2 sorption isotherms of the as-prepared CoS_2 sample based on the Brunauer-Emmet-Teller (BET) theory indicates CoS_2 nanodendrite shows low surface area with 2.41 $m^2 g^{-1}$.

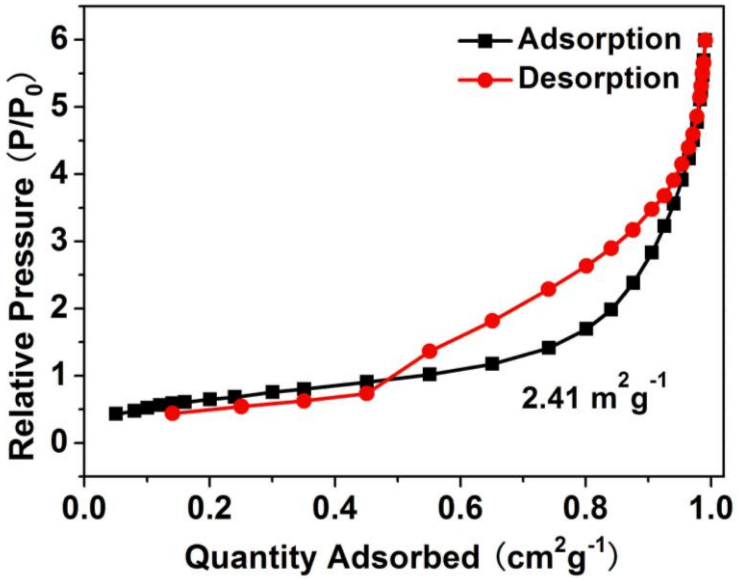

Figure 2. Nitrogen adsorption-desorption isotherm of CoS_2 nanodendrites.

For better understand the morphology and particular of the CoS_2 nanoparticles, SEM and TEM experiments were investigated, and the results are shown in Fig.3 and Fig.4, respectively. Fig. 3a-c shows the SEM images of the CoS_2 nanodendrites with low and high magnifications, which demonstrated the high yield and high quality of the CoS_2 products.

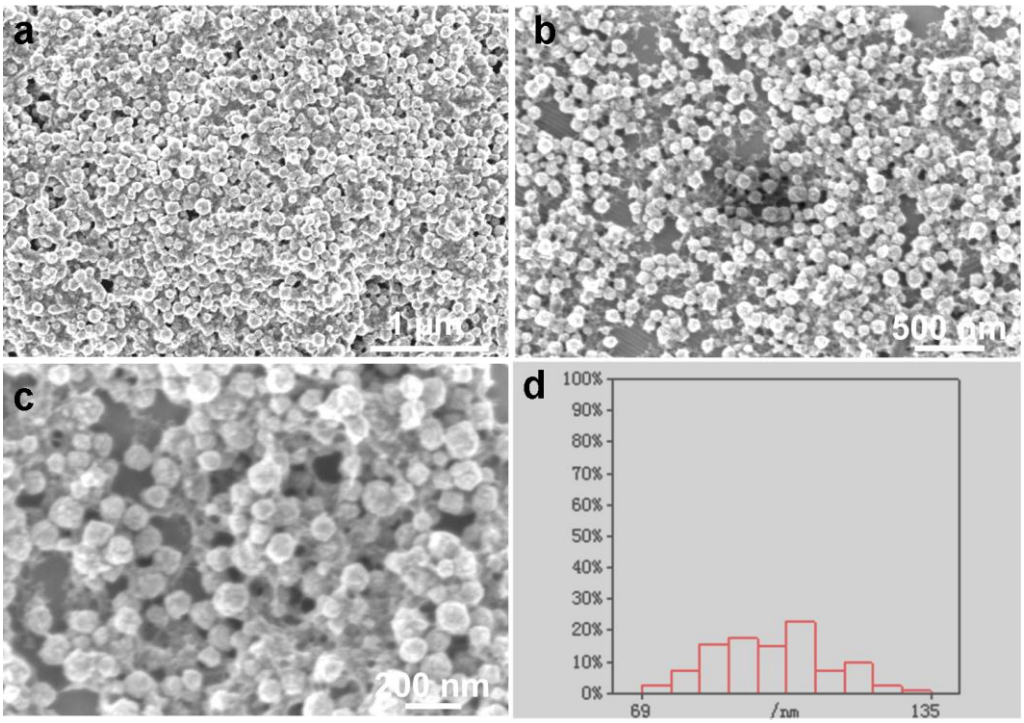

Figure 3. (a-c) FESEM image of ultrathin CoS_2 nanodendrite with different magnification prepared at 180 ^{o}C for 24 h. (d) The size distribution of CoS_2 nanodendrites.

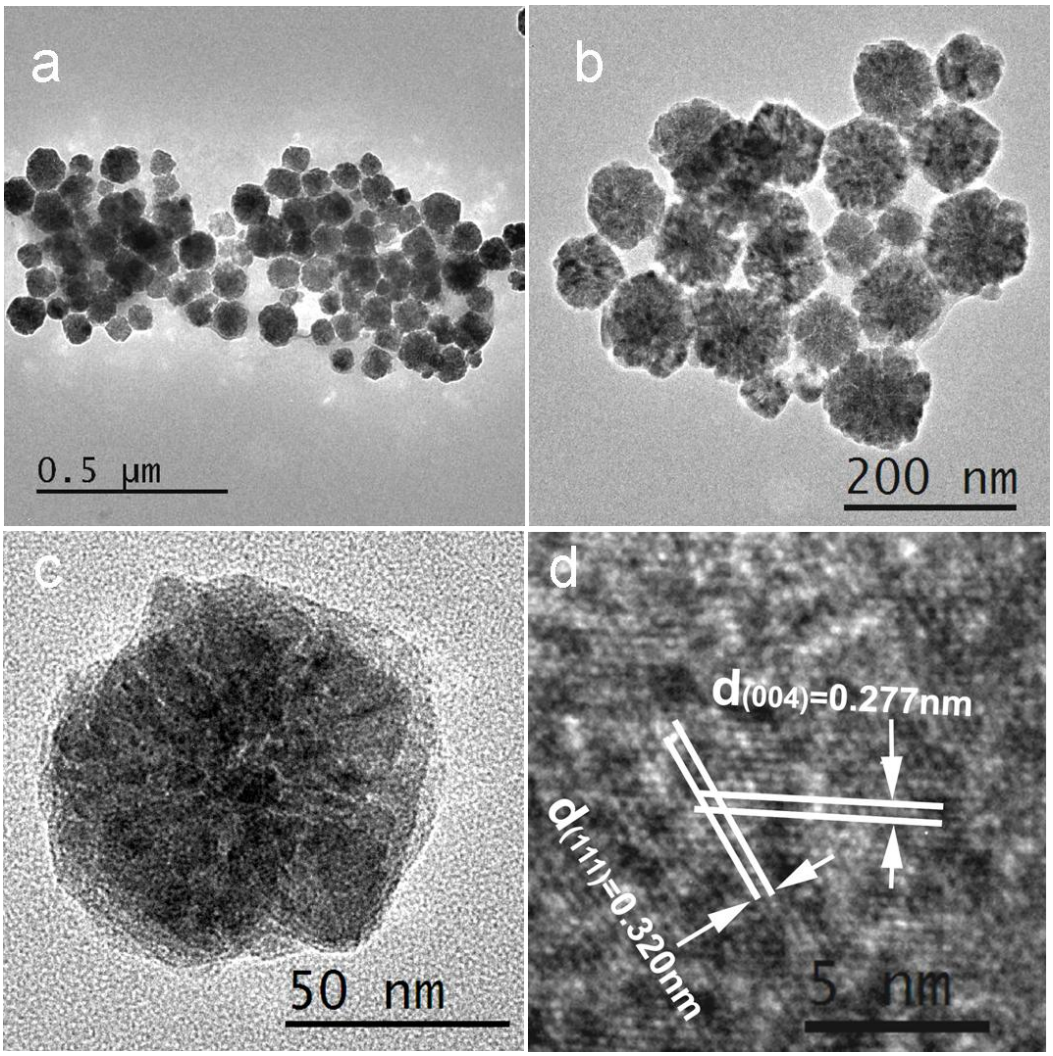

Figure 4. (a-b) Low and high mignifiacation TEM image of CoS_2 nanodendrites. (c) TEM image of a single CoS_2 nanodendrite (d) HRTEM image of a single CoS_2 nanodendrite.

Fig. 3c reveals the nearly spherical particles consist with substructure of nanosheets, which assemble to the hierachical CoS_2 nanodendrites. As illustrated in Fig. 3d, the sizes of the nanodendrites distribution in the range of 69~135 nm with an average particle size of 98.6 nm. The TEM images in Fig. 4a-c further demonstrate the harsh edge and uneven surface of as-obtained CoS_2 nanodendrites. Furthermore, Fig. 4b-c display the 3D alternately stacked structure with ultrathin nanosheets. The HRTEM image (Fig. 4d) presents the lattice fringes with interplanar distance of 0.277 and 0.320 nm, corresponding to the spacing of the (004) and (111) plane of CoS_2, respectively.

3.2 Supercapacitor performance

To explore the supercapacitor properties of the as-prepared CoS_2 nanodendrite for electrical energy storage, several electrochemical measurements were investigated in a three-electrode configuration with 2M KOH as the electrolyte.

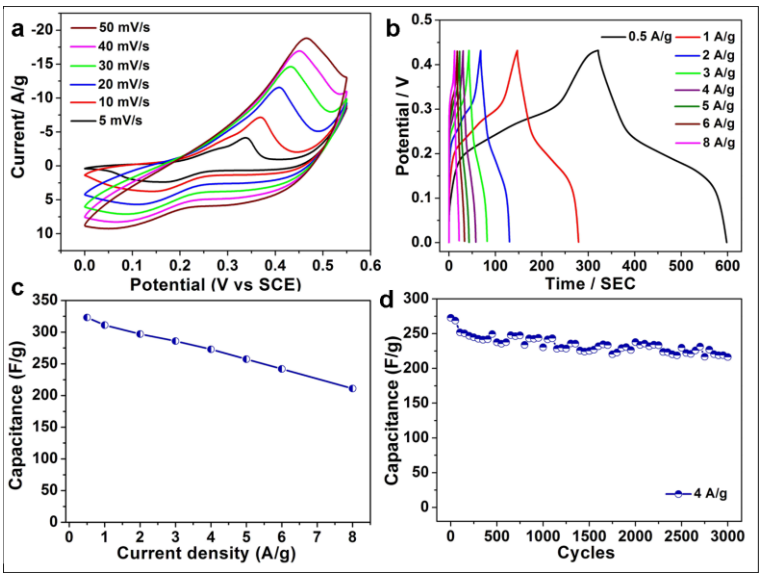

Figure 5. Electrochemical performance characterization of CoS_2 nanodendrites: (a) CV curves of CoS_2 nanodendrites modified electrode at different scan rates ranging from 5 to 50 mV s^{-1}. (b) Galvanostatic charge-discharge curves of CoS_2 with various current densities. (c) The influence of current density to discharge rate performance. (d) Cycling performance of CoS_2 at a fixed current density of 4 A g^{-1}.

Fig.5a shows the CVs curves within a 0~0.55V range at a scan rate from 5 to 50 mV s^{-1} for the CoS_2. A pair of strong redox peaks is observed in each voltammogram suggesting that the capacitance characteristics are possiblely caused by Faradaic redox reactions. At a low scan rate of 5 mV s^{-1}, the anodic peak at 0.34 V is attributed to the oxidation process, while the cathodic peak at about 0.174 V is ascribed to the reduction process. Furthermore, with the increasing scan rates, the anodic and the cathodic peaks gradually shift to higher and lower potentials, respectively. The specific capacitance of CoS_2 might be ascribed to the quasi reversible electron transfer process of the Co^{2+}/Co^{3+} redox couple in the alkaline electrolyte. The galvanostatic charge-discharge curves with various current densities are shown in Fig.5b, showing good electrochemical capacitive characteristic and reversibility of the redox reaction for the nanodendrite electrode. The specific capacitances at different current-density were calculated from the discharge curves and plotted in Fig. 5c. The CoS_2 electrode delivers the specific capacitance of 323.05, 311.06, 296.97, 285.86, 272.84, 257.41, 241.92, and 210.93 F g^{-1} at current densities of 0.5, 1, 2, 3, 4, 5, 6, and 8 A g^{-1}, respectively. In addition, the CoS_2 sample maintains the relatively high capacitance of ~65.3% when a change of the current densities from 0.5 to 8 A g^{-1} (Fig. 5c). The charge-discharge stabilization of the electrode materials were further investigated. Notably, CoS_2 nanodendrites exhibt high cyclic stability after 3000 repeating cycles with the capacitance decay of 19.78 % (80.22 %) at 4 A g^{-1} (Fig. 5d).

The specific capacitance obtained from CoS_2 nanodendrites is macthed up to or superior to the previous results of metal molybdates and transition metal sulfides, such as $CoMoO_4 \cdot 0.75H_2O$ nanorods (285 F g^{-1} at 1 A g^{-1}),[46] $MnMoO_4$ nanostructure (234 F g^{-1} at 2 A g^{-1}),[47] and hierarchical $MnMoO_4/CoMoO_4$ nanowires (187.1 F g^{-1} at 1 A g^{-1})[48], however, it is lower than that CoS_2 ellipsoids (965 F g^{-1} at 2.5 A g^{-1})[30] and $NiCoS_4$ hollow tubular structures (902 F g^{-1} at 5 A g^{-1})[49]

electrodes.

4. CONCLUSIONS

Herein, we demonstrated CoS_2 nanodendrite can be prepared by a facile solvothermal route. Enhanced specific capacitance and good cycle stability are detected in aqueous KOH electrolytes for CoS_2 nanodendrite. The results presented here indicate that the CoS_2 nanodendrite electrode shows promising applications for the development of supercapacitors in the future.

ACKNOWLEDGMENTS
Financial supports from the National Science Foundation of China (No. 21501006, 21405005, U1404208, 21301009), Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry, the Foundation of Henan educational committee (Nos. 15A150002, 15A150031, 13B150893) and the Natural Science Foundation of Shanxi Province (No. 2014011031-2) are gratefully acknowledged.

References

1. B. Dunn, H. Kamath and J.-M. Tarascon, *Science*, 334 (2011) 928.
2. D. Larcher and J-M. Tarascon, *Nature Chem.*, 7 (2015) 19.
3. H. J. Li, Y. Zhou, W. G. Tu, J. H. Ye, and Z.G. Zou, *Adv. Funct. Mater.*, 25 (2015) 998.
4. J. H. Wang, W. Cui , Q. Liu, Z. C. Xing, A. M. Asiri, and X. P. Sun, *Adv. Mater.*, 28 (2016) 215.
5. D. D. Zhu, J. L. Liu, and S. Z. Qiao, *Adv. Mater.*, 2016, DOI: 10.1002/adma. 201504766.
6. Y. M. Shi and B. Zhang, *Chem. Soc. Rev.*, 45 (2016) 1529.
7. X. H. Lu, S. L. Xie, H. Yang, Y. X. Tong and H. B. Ji, *Chem. Soc. Rev.*, 43 (2014) 7581.
8. T. Hisatomi, J. Kubota and K. Domen, *Chem. Soc. Rev.*, 43 (2014) 7520.
9. J. R. Swierk and T. E. Mallouk, *Chem. Soc. Rev.*, 42 (2013) 2357.
10. K. Zhang, X. P. Han, Z. Hu, X. L. Zhang, Z. L. Tao and J. Chen, *Chem. Soc. Rev.*, 44 (2015) 699.
11. J. B. Goodenough, *Energy Environ. Sci.*, 7 (2014) 14.
12. N.-S. Choi, Z. H. Chen, S. A. Freunberger, X. L. Ji, Y.-K. Sun, K. Amine, G. Yushin, L. F. Nazar, J. Cho and P. G. Bruce, *Angew. Chem. Int. Ed.*, 51 (2012) 9994.
13. W. F. Wei, X. W. Cui, W. X. Chen and D. G. Ivey, *Chem. Soc. Rev.*, 40 (2011) 1697.
14. G.P. Wang, L. Zhang and J. J. Zhang, *Chem. Soc. Rev.*, 41 (2012) 797.
15. X. Peng, L. L. Peng, C. Z. Wu and Y. Xie, *Chem. Soc. Rev.*, 43 (2014) 3303.
16. J. L. Liu, L. L. Zhang, H. B. Wu, J. Y. Lin, Z. X. Shen and X. W. (David) Lou, *Energy Environ. Sci.*, 7 (2014) 3709.
17. C. Z. Yuan, H. B. Wu, Y. Xie and X. W. (David) Lou, *Angew. Chem. Int. Ed.*, 53 (2014) 1488.
18. Y. F. Zhang, L. Q. Li, H. Q. Su, W. Huang and X. C. Dong, *J. Mater. Chem. A*, 3 (2015) 43.
19. K. K. Lee, W. S. Chin and C. H. Sow, *J. Mater. Chem. A*, 2 (2014) 17212.
20. Z. B. Wu, Y. R. Zhu and X. B. Ji, *J. Mater. Chem. A*, 2 (2014) 14759.
21. M. R. Gao, Y. F. Xu, J. Jiang and S. H. Yu, *Chem. Soc. Rev.*, 42 (2013) 2986.
22. X. Huang, Z. Y. Zeng, and H. Zhang, *Chem. Soc. Rev.*, 42 (2013) 1934.
23. Q. P. Lu, Y. F. Yu, Q. L. Ma, B. Chen, and H. Zhang, *Adv. Mater.*, 28 (2016) 1917.
24. D. Voiry, J. Yang and M.Chhowalla, *Adv. Mater.*, 28 (2016), DOI: 10.1002/adma.201505597.
25. J. W. Xiao, L. Wan, S. H. Yang, F. Xiao, and S. Wang, *Nano Lett.*,14 (2014) 831.
26. Y. W. Liu, C. Xiao, M. J. Lyu, Y. Lin, W. Z. Cai, P. C. Huang, W. Tong, Y. M. Zou, and Yi Xie, *Angew. Chem. Int. Ed.*, 54 (2015) 11231.

27. L. Yu, L. Zhang, H. B. Wu, and X. W. (David) Lou, *Angew. Chem. Int. Ed.*, 53 (2014) 3711.
28. T. Peng, Z. Y. Qian, J. Wang, D. L. Song, J. Y. Liu, Q. Liu, and P. Wang, J. Mater. Chem. A, 2 (2014) 19376.
29. X. Y. Yu, L.Yu, and X. W. (David) Lou, Adv. Energy Mater., 2016, 6,1501333
30. L. Zhang, H. B. Wu, and X. W. (David) Lou, *Chem. Commun.*, 48 (2012) 6912.
31. J.-C. Xing, Y.-L. Zhu, Q.-W. Zhou, X.-D. Zheng, and Q.-J. Jiao, *Electrochimica Acta*, 136 (2014) 550.
32. M. S. Faber, R. Dziedzic, M. A. Lukowski, N. S. Kaiser, Q. Ding, and S. Jin, *J. Am. Chem. Soc.*, 136 (2014) 10053.
33. J.-C. Xing, Y.-L. Zhu, M.-Y. Li, and Q.-J. Jiao, *Electrochimica Acta*, 149 (2014) 285.
34. R. C. Jin, L. X. Yang, G. H. Li, and G. Chen, *J. Mater. Chem. A*, 3 (2015) 10677.
35. Q. H. Wang, L. F. Jiao, Y. Han, H. M. Du, W. X. Peng, Q. N. Huan, D. W. Song, Y. C. Si, Y. J. Wang, and H. T. Yuan, *J. Phys. Chem. C*, 115 (2011) 8300.
36. W.W. Chen, T. T. Li, Q. Hu, C. P. Li, and H. Guo, *Journal of Power Sources*, 286 (2015) 159.
37. H. C. Zhang, Y. J. Li, T. H. Xu, J. B. Wang, Z. Y. Huo, P. B. Wan, and X. M. Sun, *J. Mater. Chem. A*, 3 (2015) 15020.
38. Z. Shadike, M.-H. Cao, F. Ding, L. Sang, and Z.-W. Fu, *Chem. Commun.*, 51 (2015) 10486.
39. B. Wang, J. Park, D. W. Su, C. Y. Wang, H. Ahn, and G. X. Wang, J. Mater. Chem., 22 (2012) 15750.
40. H. C. Zhang, Y. J. Li, G. X. Zhang, T. H. Xu, P. B. Wan, and X. M. Sun, J. Mater. Chem. A, 3 (2015) 6306.
41. J. Xie, S. Y. Liu, G. S. Cao, T. J. Zhu, and X. B. Zhao, *Nano Energy*, 2 (2013) 49.
42. S. Amaresh, K. Karthikeyan, I.-C. Jang, and Y. S. Lee, *J. Mater. Chem. A*, 2 (2014) 11099.
43. J.-C. Tsai, M.-H. Hon, and I.-C. Leu, *RSC Adv.*, 5 (2015) 4328.
44. Y. Ji, X. Y. Liu, W. Liu, Y. Wang, H. D. Zhang, M. Yang, X. F. Wang, X. D. Zhao, and S. H. Feng, *RSC Adv.*, 4 (2014) 50220.
45. C. Zhao, D. Q. Li, and Y. J. Feng, *J. Mater. Chem. A*, 1 (2013) 5741.
46. M. Mandal, D. Ghosh, S. Giri, I. Shakir, and C. K. Das, *RSC Adv.*, 4 (2014) 30832.
47. D. Ghosh, S. Giri, M. Moniruzzaman, T. Basu, M. Mandala, and C. K. Das, *Dalton Trans.*, 43 (2014)11067.
48. L. Q. Mai, F. Yang, Y. L. Zhao, X. Xu, L. Xu, and Y. Z. Luo, *Nat. Commun.*, 2 (2011) 381.
49. Y. M. Chen, Z. Li, and X. W. (David) Lou, *Angew. Chem. Int. Ed.*, 54 (2015) 10521.