International Journal of ELECTROCHEMICAL SCIENCE www.electrochemsci.org

Synthesis of Nitrogen and Sulfur Co-Doped Sisal Fiber Carbon and Its Electrochemical Performance in Lithium-Ion Battery

Denglei Wang¹, Kaiyou Zhang¹, Lei Liao^{1,2,*}, Shuoping Chen¹, Aimiao Qin^{1,*}

 ¹ Key Lab New Processing Technology for Nonferrous Metals & Materials Ministry of Education, College of Materials science & engineering, Guilin University of Technology, Guilin, China
²Guangxi Key Laboratory of Environment Pollution Control Theory and Technology, College of Envir onmental Science and Engineering, Guilin University of Technology Guilin, China
*E-mail: <u>fangqiu2001@163.com</u> (Lei Liao), <u>2005032@glut.edu.cn</u> (Aimiao Qin)

Received: 10 October 2018 / Accepted: 6 November 2018 / Published: 30 November 2018

Heteroatoms substitution doping carbon materials were proved to be a useful strategy to tailor their physicochemical properties when it comes to energy application, here we present the fabrication of nitrogen and sulfur dual- doped sisal fiber carbon via a facile hydrothermal process followed by pyrolysing with sulphamic acid as the nitrogen and sulfur source. As an electrode material for lithiumion battery (LIB), the nitrogen and sulfur co-doped sisal fiber carbon delivers a specific capacity of 525 mAh/g at 0.05 A/g and 220 mAh/g at 1 A/g after 50 circles, revealing a high specific capacity and good cycle stability. The electrochemical performance of carbon material doped with N and S at different amount of dopant is better than the un-doped one and it would be a potential green and low-cost anode candidate for LIB.

Keywords: sisal fiber carbon; nitrogen and sulfur co-doping; hydrothermal synthesis; lithium-ion battery

1. INTRODUCTION

Carbonaceous materials as one of the most suitable candidates, with the merits of renewable, low-cost and availability, hitherto have been well-studied in the scientific community such as sensors and photovoltaic as well as adsorbent [1-3], so it has potential to be applied in many aspect of daily life. Whereas the fact is that pure carbon materials cannot always match the increasing requirements for certain applications. In order to access vary of applications, tremendous effects have been made to obtain the fine-tuning of carbon materials. It is worth mentioning that the introduction of heteroatoms, such as nitrogen, sulfur and boron into carbonaceous materials is a facile and useful method for tailoring and

enhancing their physicochemical properties [4-6]. When it comes to applications, such as electrode materials for energy storage, catalysis in fuel cells, CO₂ capture, oxygen reduction reaction (ORR) and so on, many studies have been performed [7, 8]. To this day, there have been a variety of strategies to introduce heteroatoms into carbon materials, mainly including in situ doping method that direct carbonization of heteroatom-containing materials (acetonitrile, pyrrole or polyaniline) as well as post-treatment that is to say the carbon texture is yielded to some chemical agents (ammonia, urea or amines) at certain temperatures.

With the intensive interest at the broadening the application range of carbonaceous materials in energy storage, researchers have made great efforts and obtained certain achievements in the past few years. Chen [9] used corn starch as raw materials to fabricate micro-sized porous carbon spheres (PCSs) by series of procedures such as enzymolysis, pre-oxidation, and carbonization, as electrode materials they exhibited an superior rate capability with a value of 150 mAh/g at a current density of 20 A/g. Incorporation of guest atoms into the carbon backbone is considerable to mediate their electron-donor properties and accordingly tailor the electrochemical performance of their surface [10, 11]. The presence of doped heteroatom can decrease the charge transfer resistance and improve the surface wettability of electrolyte, and make adsorption of ions from the electrolyte become easier to enhance the specific capacitance [12]. Typical heteroatoms including nitrogen [6, 13], phosphorus [4, 11], sulfur [14, 15] and boron [16, 17] can be combined in a single- or dual-doped and even ternary-doped manner to tune the carbon materials.

Up to know, among the elements for doping carbon, nitrogen is by far the most comprehensively investigated heteroatom due to several reasons. Above all, as a "neighbour" of carbon on the periodic table, it is chemically relatively comfortable to combine the two different types of atoms together and substituting one carbon atom with one nitrogen atom in the carbon matrix. For another, nitrogen atom has an atomic radius similar to that of carbon atom, hence the significant lattice mismatch is avoided. Finally, doped with nitrogen element can induce an n-type electron application to the carbon skeleton, similar to typical semiconducting materials, which makes the C-N structure have potential applications in the area of nano-electronic devices [13]. Indeed, worldwide researchers have made significant efforts on the fabrication concerning N-doped carbon materials, tremendous examples suggest that nitrogen atoms induce favorable pseudo-capacities when applied in supercapacitors, especially relying on the protonation of pyridinic nitrogen atoms at graphitic edges [18], furthermore, nitrogen doping into carbon materials for energy storage can enhance the intercalation properties and improve the specific capacity.

Supplementing nitrogen as an adulterant, sulfur is receiving extensively attention in present carbon materials investigation [19]. Mesoporous carbon fibres doped with S were prepared by carbonization of sucrose using MgSO₄-containing porous whiskers as templates and S source [20]. As electrodes for supercapacitors, the specific capacitance of the S-doped mesoporous carbon fibres was significantly increased as the S content increasing, reaching 221 F/g at the scan rate of 10 mV/s with an area-normalized capacitance of 38 mF/cm². As a dopant, sulfur serves as a donor of electrons and manifests various kinds of changes at the electronic density of states when compared with N or B doping, and the S-doped carbons have more disorders and better conductivity as compared to the pristine carbons.

By contrasting with single heteroatom substitution that barely enhances one aspect of properties, dual-doping can enhance entire performance of the materials by the reason of the synergetic effect [21, 22]. Therefore, great efforts have been made in investigating the multi-heteroatom doping in recent years. Carbon materials binary doping with sulfur and nitrogen have been applied into oxygen reduction reaction (ORR) [23], and several researches in the fields of energy storage materials have been reported. Liu [24] prepared a N, P-dually doped porous carbon (NPC) material using a thermochemical self-doping process and a renewable hydrophyte biomass. As electrodes for supercapacitors, the NPC revealed a maximum capacitance of 257 F/g and energy density of 19.0 Wh/kg and only 3% capacitance loss after 6000 times of cyclic use. A range of papers presented synthesis of carbons materials dually doped with nitrogen and sulfur stemed from biomass and amino acids [25, 26]. Reproducible and inexpensive biomass is a promising ingredient for fabrication of carbons modified with guest atoms. Deliberately selecting an eligible biomass as a precursor, a range of heteroatoms can be co-doped in the ultimate carbon-based materials.

Sisal fiber, extracted from the leaves of the sisal plant, is a hard fiber. As one of the mostly natural and easily cultivated plants, sisal fiber is composed of 65.8% of cellulose, 12.0% of hemicellulose, 9.9% of lignin and some trace elements. Besides, it is a sort of renewable plant with excellent property such as durability, stiffness, ability to stretch, which is extensively applied in many other respects ranging from textiles to crafts [27] and from reinforced materials [28] to electrode materials [29, 30].

Herein, the aim of this work is to fabricate expectant material related to sulfur and nitrogen codoped sisal fiber carbon using a simple hydrothermal method with stress on the employ of cheap and bio-based precursors. The sulfamic acid was chosen as nitrogen and sulfur source since not only it contains N and S element in its functional group, but also it is an inexpensive and environmental-friendly substance. The obtained carbon materials with nitrogen content of about 3.0-4.5 wt% and sulfur content of 0.7-0.9 wt% can accordingly be acquired. Post-pyrolysis of the carbonaceous hydrothermal carbonization products is in favor of additional control over material stability and functionality [19].

2. EXPERIMENTAL

2.1 Preparation of sisal fiber carbon (SFC)

Briefly, the raw sisal fibers were washed with deionized water (DI) for several times to removal impurities, and then were dried at 60 °C for 8 h in an oven, the dried sisal fibers following were cut into pieces with the length of 2 cm. Subsequently, 2 g of sisal fibers were put into a 100ml Teflon-lined stainless autoclave containing 75ml of 1.5 M HCl solution followed by hydrothermal treatment at 180 °C for 16h. When cooled down to room temperature naturally, the samples were washed repeatedly with DI water until the pH value of the filtrate was equal to 7 and dried at 60°C for 12h. Afterwards, the product was pyrolyzed in a tubular furnace under argon atmosphere (700 °C for 0.5h, heating rate: 3°C/min), finally the sisal fiber carbon was prepared.

2.2 Synthesis of N, S co-doping SFC (NS-SFC)

Sulfamic acid (SFA) was chosen as both the N and S precursors. Typically, 0.12g of SFC powder was immersed in a 50ml of DI water containing different mass of sulfamic acid (1g, 2g, 3g) in a 100ml Teflon-lined autoclave with magnetic stirring for 1h at 60°C followed by a hydrothermal treatment at 140°C for 12h. After finishing the process of hydrothermal treatment, the supernatant was reserved to uniformly mixture with the bottom precipitate and dried at 60 °C for 10h before proceeding the next step. Carbonization was implemented at 750 °C for 1h under a nitrogen atmosphere, and the resultant samples prepared with 1g, 2g and 3g of SFA were named as NS-SFC-n (n=1, 2, 3) respectively.

2.3 Material characterizations

The morphology of as-prepared samples was characterized using scanning electron microscopy (FESEM, S-4800). Powder X-ray diffraction (XRD, X'Pert PRO, PANalytical B.V.) was employed to investigate the crystalline phase of as-prepared materials. X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermo Electron Co) with Al K_{α} line as the excitation source (radiation) was used to reveal the surface chemical species of the samples. Raman spectrum was taken on the graphitized feature of the samples using a DXR Raman system with 532 nm excitation laser.

2.4 Electrochemical performance

The electrochemical performance was evaluated using CR2025-type coin cells assembled in an Ar-filled glove-box (Super 1220/750, Mikrouna). The active material was fabricated by mixing 80 wt% of as-obtained NS-SFC-n (n=1, 2, 3) with 10 wt% of poly (vinylidene fluoride) and 10 wt% of acetylene black conductive carbon, and then it was uniformly coated onto a Cu foil and dried at 110 °C for 12 h in a vacuum oven. The lithium plate was used as both counter and reference electrodes, the celgard 2500 polypropylene membrane film serves as the separator, and 1 M LiPF6 in ethylene carbon (EC) and dimethyl carbonate (DMC) mixture with a 1:1 ratio (v/v) was used as the electrolyte. Cyclic voltammetry (CV) measurements were conducted between 0.01 and 3.0 V (vs. Li/Li⁺) at a scan rate of 0.2mV/s on an electrochemical work station. (CHI-760D) The galvanostatic charge-discharge tests were performed at room temperature with the voltage range between 3.0 V and 0.01 V (vs. Li/Li⁺) on a NEWARE battery test system.

3. RESULT AND DISCUSSION

The morphology evolution of the SFC was characterized by SEM observations. As is shown in Fig. 1a, the pristine sisal fiber pyrocarbon without hydrothermal treatment has a rather smooth surface with a diameter of about 4 μ m. While the SFC exists a great deal of microspheres sticking to the rough surface that maybe result from the reunion of lignin [31, 32] or the formation of Pseudo-lignin [33] (Fig. 1b₁, b₂). The main chemical components that make up the cell walls of sisal fibers such as cellulose,

hemicellulose, lignin and the relationship among them are complex. That is, cellulose molecular chains gather into ordered microfiber bundles and exist in the cell wall, which palys a supporting role on the whole cell wall skeleton. As a filling material, hemicellulose permeates the microfiber in an amorphous state to increase the rigidity of cell wall. Lignin, as a crusting material, binds cellulose and hemicellulose together to form a solid cell wall structure similar to the reinforced concrete. This compact structure seriously restricts the efficient utilization of sisal fibers and the high value transformation of chemical components. Therefore, the acid hydrothermal pretreatment for sisal fiber was needed to destroy the crystal structure of the cellulose, degrade the hemicellulose, make lignin expand and eliminate its protective effect on cellulose in order to increase the porosity and specific surface area of SFC [34].



Figure 1. SEM images of pristine sisal fiber pyrocarbon (a1, a2) and SFC (b1, b2)



Figure 2. SEM and EDS images for NS-SFC-1 (a1, a2, a3), NS-SFC-2 (b1, b2, b3), NS- SFC-3 (c1, c2, c3)

Fig. 2 shows the morphological evolutions of N, S-dually doped carbon obtained at various amount of the dopant. The identical elemental composition and the content of N, S of N,S-SFC and SFC are compared from EDS, as shown in Table 1. It is observed that the feature of SFC is mainly consist of tubular carbon (Fig.1b), however the tubular structure of SFC was destroyed and the amount of microspheres increased with the increasing of the content of nitrogen and sulfur (Fig.2a-c).The agglomeration of microspheres can be seen when further increased the amount of the dopant (Fig.2c). Compared with N,S-SFC-1 and N,S-SFC-3, the particle size distribution of microspheres in N,S-SFC-2 (3.77 wt% of N and 0.72 wt% of S) is much more uniform, and the average diameter is about 100nm.

Weight(wt%)	С	Ν	Ο	S
SFC	91.67		8.18	
NS-SFC-1	91.38	2.99	4.90	0.73
NS-SFC-2	87.93	3.77	7.58	0.72
NS-SFC-3	89.94	4.49	4.66	0.91

Table 1. Element analysis data (wt%) for the SFC and NS-SFC-n (n=1,2,3)

The degree of crystallization concerning the as-prepared specimens was investigated via X-ray diffraction (XRD) and the results were shown in Fig. 3a. Two broad diffraction peaks at around 24° and 45° are responsible for the (002) and (100) planes, indicting a disordered structure and a limited degree of graphitization in the amorphous carbons respectively. Notably, the (002) diffraction peak of the NS-SFC-n (n=1, 2, 3) samples slowly moved to the direction of high angle compared with SFC with the increasing content of N and S elements, revealing the interlayer spacing of the sulfur and nitrogen doped materials are much larger than in graphite, which indicates that the materials doped with N and S elements contain many structural defects.



Figure 3. XRD (a) and Raman spectra (b) of SFC and NS-SFC obtained at different amount of dopant

The structure characteristics of the samples were further evaluated by the Raman spectra, as shown in Fig. 3b, all the samples possess two pronounced peaks at around 1340 and 1580 cm⁻¹, corresponding to the D-band (associated with the sp³ defective) and the G-band (sp²-hydriized carbon) of the prepared materials. The integral intensity ratio of the D band and G band (I_D/I_G) reveals the level of disorder degree of SFC and NS-SFC-n (n=1, 2, 3), and the calculated value of SFC, NS-SFC-1, NS-SFC-2 and NS-SFC-3 is 0.663, 0.955, 1.032, and 1.037, respectively. The results imply that the I_D/I_G ratio subtly changes with increasing the amount of the doping agent, obviously there is not much difference between NS-SFC-2 and NS-SFC-3. Suggesting the increase of defects result from the introduction of the nitrogen and sulfur element [35], which is consistent with the result of XRD analysis.

The XPS was implemented to determine the ingredient as well as differentiation between the surface functional groups of the doping materials. Taking NS-SFC-2 as an example, it is primarily consisted of carbon, nitrogen, oxygen and sulfur (Fig.4a), respectively. Fig. 4b presents the high-resolution spectra of C1s which can be de-convoluted into three peaks with binding energies at 284.6, 285.7 and 288.7 eV corresponding to the C-C/C=C, C-N/C-S and C=N/O-C=O bonds, respectively [36]. As is shown in Fig. 4c, the spectra of N1s can be fitted by four peaks, which can be ascribed to the existence of N-6 bond (398.2 eV), N-5 (400.3 eV), N-X (pyridine N-oxygen) (402.6) and N-O (405.6) in the as-obtained NS-SFC-2 [37]. The high-resolution spectrum of S2p in Fig. 4d confirms the presence of C-S-C units, which can be divided into two peaks centered at 163.8 eV (2p^{3/2}) and 164.9 eV (2p^{1/2}) [38]. Notably, there is a broad peak at 168 eV in Fig. 4d indicating the existence of oxidized S [39].



Figure 4. XPS survey spectrum (a), XPS spectra of C1s (b), N1s (c) and S2p (d) for NS-SFC-2

A typically cyclic voltammogram curve of NS-SFC-2 was revealed in Fig. 5a. Two cathodic peaks appeared at about 0.6V and 1.6V during the first cycle scan, and then disappeared during the following cycles, which can be attributed to the formation of a solid electrolyte interphase (SEI) layer and the electrolyte decomposition as well as the irreversible reaction between lithium and surface functional groups[40]. In addition, the electrochemical performance of the sample was further evaluated by galvanostatic charge/discharge at a current density of 0.05A/g, as shown in Fig. 5b, the first discharge capacity is up to 1274mAh/g, after 50 charge/discharge circle, the capacity remains 525 mAh/g, indicating the superior circle stability.



Figure 5. (a) CV curves of NS-SFC-2; (b) Charge-discharge curve of NS-SFC-2 at a current density of 0.05A/g

Moreover, the comparison on the cyclic performance of NS-SFC-n (n=1, 2, 3) and SFC is firstly made at the current density of 0.05A/g. It is apparent that the cyclic performance of all of NS-SFC is superior to that of SFC (As seen in Fig. 6a). It is noted that the reversible capacity of NS-SFC-2 can reach 525mAh/g after 50 circles, which is better than that of NS-SFC-1 (392mAh/g) and NS-SFC-3 (464mAh/g). The nitrogen and sulfur co-doped carbon as electrode material also shows excellent cycling stability at a high current density of 1 A/g. As shown in Fig. 6b, although the capacity decreases with the increase of cycle number, it retains a specific capacity of 220 mAh/g at a high current density of 1A/g for NS-SFC-2 sample, which is similar with the NS-SFC-3 (226mAh/g) and higher than NS-SFC-1 (181mAh/g) after 50 cycles, all of them are much higher than SFC. We further compare NS-SFC with other similar carbons in literatures and the results are shown in Table 2. It can be seen that the NS-SFC-2 electrode in this work exhibits a higher reversible capacity after 50 circles both at low current and high current density.

What is more, the rate capability of NS-SFC-n (n=1, 2, 3) and SFC were illustrated in Fig. 6c. The samples were first recycled at 0.05 A/g for 5 cycles, and then the current density was increased stepwise to 2 A/g for 5 cycles at each rate. At the current density of 0.05 A/g, the discharge capacity of NS-SFC-2 is 618mAh/g, which is higher than that of NS-SFC-1 (480 mAh/g) and NS-SFC-3 (500 mAh/g), and all of them are higher than that of SFC (151 mAh/g). Even at a relative high current density of 1 and 2 A/g, the discharge capacity of NS-SFC-2 still retained 315 and 246 mAh/g respectively, which is larger than that of NS-SFC-3 (256 mAh/g and 202 mA/g).

When the current density return to 0.05A/g after cycling at different current densities, the specific capacity of NS-SFC-2 can still be recovered to 500 mAh/g, which is larger than that of NS-SFC-1 (445 mAh/g) and NS-SFC-3 (483 mAh/g). All of them are much superior to that of SFC (163 mAh/g) suggesting the highly stable cycling performance and excellent reversibility.



Figure 6. The cycling performance of NS-SFC-n (n=1, 2, 3) and SFC at current density of 0.05A/g (a) and 1A/g (b); rate capabilities cycled 5 times at each current density from 0.05A/g to 2A/g (c)

Table 2. Comparison of NS-SFC-2 and other carbon materials derived from different precursors

Carbon source	Reversible capacity (mAh/g)	Current density (mAh/g)	Reference
Turbostratic carbon	500	37.2	[41]
Wheat stalk	433.7	37	[42]
Phenolic formldehyde	480	50	[43]
Human hair	410	372	[44]
Garlic peel	360	500	[45]
Sisal fiber	525	50	This work
Sisal fiber	220	1000	This work

The electrochemical impedance spectroscopy (EIS) was employed to understand the merit of NS-SFC-n (n=1, 2, 3) as electrode materials for superior performance in LIBs. As shown in Fig. 7, the Nyquist plots of all samples consist of a depressed semicircle in the high-middle frequency region associated with the resistance for lithium ion permeate the SEI film and the semicircle in the middle frequency related to the charge transfer process, and the oblique line in the low frequency region corresponding to lithium ion diffusion in the carbon electrode. As seen from the Nyquist plots, it can be found that although the radius of the semicircle of NS-SFC-3 is smaller than that of NS-SFC-1 and NS-SFC-2 electrodes, the apparent difference is not observed. Compared with SFC, the radius of semicircle of NS-SFC-n (n=1, 2, 3) electrodes is much smaller, indicating a smaller charge transfer resistance. This is strong evidence that the N, S-dual doped SFC possess the superior conductivity.



Figure 7. Nyquist plots of NS-SFC-n (n=1, 2, 3) and SFC at open circuit potential

The higher electrochemical performance of the N, S co-doped SFC can be attributed to the strongly bonded heteroatoms in SFC. N-doping can improve not only the conductivity but the surface wettability of the carbon material, whereas the S-doping is regarded as increasing the interlayer distance, and the amount of micropores. Carbon doped with sulphur also increases the content of the co-dopant-N, which leads to more electrons being introduced into the graphite layer. Qiao [23] discovered that through the calculation of density functional theory, a synergistic effect of combined nitrogen and sulfur-doping was determined, based on the changes of spin density and charge of the double-doped material at the different parts. Electrochemical result unfolds that not only large reversible capacity but also excellent rate performance as well as excellent conductivity can be achieved for N, S co-doped SFC compared with un-doped counterpart.

4. CONCLUSIONS

In summary, sulphamic acid was successfully employed as a dopant to fabricate N, S co-doped SFC via hydrothermal process and followed by heat treatment. When N, S co-doped SFC is employed

as anode material for LIBs, it shows excellent electrochemical performance such as high reversible capacity, cycling stability and rate capability. It delivered a high specific capacity of 525 mAh/g at 0.05A/g and 220 mAh/g at 1A/g after 50 circles. The extremely improved electrochemical properties can be ascribed to synergetic effects of N and S atoms. The naturally renewable biomass, facile preparation process and outstanding electrochemical performance would make N, S co-doped SFC be a promising LIB anode material.

ACKNOWLEDGEMENTS

This work was supported by the National Natural Science Foundation of China (No.51564009, 51468011), and by the Natural Science Foundation of Guangxi province (No.2015GXNSFDA139035).

References

- 1. X. Huang, Z. Yin, S. Wu, X. Qi, Q. He, Q, Zhang, Q. Y, F. Boey and H. Zhan, *Small*, 7 (2011) 1876–1902.
- 2. R. H. Baughman, A. A. Zakhidov and W. A. D. Heer, Science, 297 (2013) 787-792.
- 3. N. Kannan and M. M. Sundaram, Dyes Pigments, 51 (2001) 25 40.
- 4. J. P. Paraknowitsch and A. Thomas, Energy Environ. Sci., 6 (2013) 2839-2855.
- W. J. Si, J. Zhou, S. M. Zhang, S. J. Li, W. Xing and S. P. Zhuo, *Electrochim. Acta.*, 107 (2013) 397-405.
- 6. Y. F. Deng, Y. Xie, K. X. Zou and X. L. Ji, J. Mater. Chem. A, 4 (2015) 1144-1173.
- 7. F. Jaouen, M. Lefèvre, J. P. Dodelet and M. Cai, Phys. Chem. B, 110 (2006) 5553-5558.
- 8. K. Gong, F. Du, Z. Xia, M. Durstock and L. Dai, Science, 323 (2009) 760-764.
- 9. M. Chen, C. Yu, S. Liu, X. Fan, C. Zhao, X. Zhang and J. Qiu, Nanoscale, 7 (2015) 1791-1795.
- 10. J. Ou, Y. Z. Z, L. Chen, Q. Zhao, Y. Meng, Y. Guo and D. Xiao, J. Mater. Chem. A, 3 (2015) 6534-6541.
- 11. J. Q. Wang, Z. Z. Yang, F. S. Pan, X. W. Ziu, X. W. Liu, L. Gu and Y. Yu, *RSC Advances*, 5 (2015) 55136 -55142.
- 12. S. M. Li, S. Y. Yang, Y. S. Wang, C. H. Lien, H. W. Tien, S. T. Hsiao, W. H. Liao, H. P. Tsai, C. L.Chang and C.C. Ma, *Carbon*, 59 (2013) 418-429.
- 13. K. N. Wood, R. O'Hayre and S. Pylypenko, Energy Environ. Sci., 7 (2014) 1212-1249.
- 14. W. Kiciński, M. Szala and M. Bystrzejewski, Carbon, 68 (2014) 1-32.
- 15. X. Yu and H. S. Park, Carbon, 77 (2014) 59-65.
- 16. D. W. Wang, F. Li, Z. G. Chen, G. Q. Lu and H. M. Cheng, Chem. Mater., 20 (2008) 7195-7200.
- 17. C. N. R. Rao, K. Gopalakrishnan and A. Govindaraj, Nano Today, 9 (2014) 324-343.
- 18. G. Lota, K. Lota and E. Frackowiak, Electrochem. Commun., 9 (2007) 1828-1832.
- 19. S. A. Wohlgemuth, F. Vilela, M. M. Titirici and M. Antonietti, Green Chem., 14 (2012) 741-749.
- 20. X. L. Ma, G. Q. Ning, Y. F. Kan, Y. M. Ma, C. L. Qi, B. Chen, Y. F. Li, X. F. Lan and J. S. Gao, *Electrochim.Acta*. 150 (2014) 108-113.
- 21. P. F. Fulvio, J. S. Lee, R. T. Mayes, X. Wang, S. M. Mahurin and S. Dai, *Phys. Chem. Chem. Phys*, 13 (2011) 13486-13491.
- 22. S. Wang, E. Iyyamperumal, A. Roy, Y. Xue, D. Yu and L. Dai. *Angew. Chem. Int. Ed.*, 50 (2011) 11756-11760.
- 23. J. Liang, Y. Jiao, M. Jaroniec and S. Z. Qiao, Angew. Chem., 51 (2012) 11496-11500.
- 24. W. J. Liu, K. Tian, L. L. Ling, H. Q. Yu and H. Jiang, Environ. Sci. Technol., 50 (2016) 12421-12428.
- 25. H. C. Chang, S. H. Park and S. I. Woo, Green Chem., 13 (2011) 406-412.
- 26. C. H. Choi, M. W. Chung, S. H. Park and S. I. Woo, Phys. Chem. Chem. Phys., 15 (2013) 1802-1805.

- 27. Y. Li, Y. W. Mai and L. Ye, Compos. Sci. Technol., 60 (2000) 2037-2055.
- 28. A. C. Milanese, M. O. H. Cioffi and H. J. C. Voorwald, Compos. Part B Eng., 43 (2012) 2843-2850.
- 29. Z. W. Yang, H. J. Guo, X. H. Li, Z. X. Wang, Z. L. Yan and Y. S. Wang, *J. Power Sources*, 329 (2016) 339-346.
- 30. X. L. Yu, K.Y. Zhang, N. Tian, A.M. Qin, L. Liao, R. Du, C. Wei, Mater. Lett., 142 (2015) 193-196.
- M. J. Selig, S. Viamajala, S. R. Decker, M. P. Tucker, M. E. Himmel and T. B. Vinzant, *Biotechnol. Progr.*, 23 (2007) 1333-1339.
- 32. B. S. Donohoe, S. R. Decker, M. P. Tucker, M. E. Himmel and T. B. Vinzant, *Biotechnol. Bioeng.*, 101 (2008) 913–925.
- 33. P. Sannigrahi, H. K. Dong, S. Jung and A. Ragauskas, Energy. Environ. Sci., 4 (2011) 1306-1310.
- 34. N. Mosier, C. Wyman, B. Dale, R. Elander, Y. Y. Lee, M. Holtzapple and M. Ladisch, *Bioresour. Technol.*, 96 (2005) 673-686.
- 35. W. H. Yu, H. L. Wang, S. Liu, N. Mao, X. Liu, J. Shi, W. Liu, S. G. Chen and X. Wang, *J. Mater. Chem. A*, 4 (2016) 5973-5983.
- 36. J. Shen, T. Zhang, Y. Cai, X.Y. Chen, S.M. Shang and J. Li, New J. Chem., 41 (2017) 11125-11137.
- 37. Y. Q. Chang, F. Hong, C. X. He, Q. L. Zhang and J. Liu, Adv. Mater., 25 (2013) 4794-4799.
- 38. Y. Q. Dong, H. C. Pang, H. B. Yang, C. X. Guo, J. W. Shao, Y. W. Chi, C. M. Li and T. Yu, *Angew. Chem. Inte. Edi.*, 52 (2013) 7800-7804.
- 39. Y. A. Zhu, C.Y. Cao, W. J. Jiang, S. L. Yang, J. S. Hu, W. G. Song and L. J. Wan, *J. Mater. Chem. A*, 4 (2016) 18470-18477.
- 40. T. Yang, T. Qian, M. Wang, X. Shen, N. Xu, Z. Sun and C. Yan, Adv. Mater., 28 (2016) 539-545.
- 41. D. Bhattacharjya, H. Y. Park, M. S. Kim, H. S. Choi, S. N. Inamdar and J. S. Yu, *Langmuir*, 30 (2014) 318-324.
- 42. X.Y. Zhou, F. Chen, T. Bai, B. Long, Q.C. Liao, Y.P. Ren and J. Yang. *Green Chem.*, 18 (2016) 2078-2088.
- 43. F. F. Wang, R. R. Song, H. H. Song, X. H. Chen, J. S. Zhou, Z. K. Ma, M. C. Li and Q. Lei, *Carbon*, 81(2015) 314-321.
- 44. K. R. Saravanan, N. Kalaiselvi, Carbon, 81 (2015) 43-53.
- 45. V. Selvamani, R. Ravikumar, V. Suryanarayanan, D. Velayutham and S. Gopukumar, *Electrochim. Acta*, 190 (2016) 337-345.

© 2019 The Authors. Published by ESG (<u>www.electrochemsci.org</u>). This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (http://creativecommons.org/licenses/by/4.0/).