Synthesis and electrochemical properties of Co$_3$O$_4$ nanoparticles by hydrothermal method at different temperatures

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Abstract. In this work, Co$_3$O$_4$ nanoparticles were synthesized by hydrothermal method at different temperatures. The synthesized Co$_3$O$_4$ nanoparticles were characterized using transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectrometer (XPS) and nitrogen adsorption-desorption. The Co$_3$O$_4$ nanoparticles prepared at the hydrothermal temperature of 140 $^\circ$C and at the annealing temperature of 350 $^\circ$C have a shorter crystal spacing distance associated to the (220) crystal planes, larger BET surface area and more bivalent cobalt on the surface than these of Co$_3$O$_4$ nanoparticles prepared at higher hydrothermal temperature or higher annealing temperature. The supercapacitor performances of synthesized Co$_3$O$_4$ nanoparticles were analysed by cyclic voltammograms (CVs), Galvano static charge/discharge (GCD) and the electrochemical impedance spectroscopy (EIS) in 6 M KOH aqueous electrolyte solution. The Co$_3$O$_4$ nanoparticles produced at lower hydrothermal temperature and the annealing temperature of Co$_3$O$_4$ nanoparticles, they can be relatively low cost in favour of a promising candidate for electrochemical supercapacitors.

1. Introduction

Given rises in environmental pollution and rapid consumption of traditional fossil fuel energy resources, it is extremely urgent to explore more efficient, clean, and low-cost energy conversion/storage resources with high energy and power capacity [1-3]. Supercapacitors have attracted considerable attentions for their high power density, long cycle life and fast charge-discharge capability [4-6]. The core of supercapacitors is the electrode materials, which directly dominates the performance of energy storage. Transition metal oxides such as MnO$_2$, NiO, RuO$_2$ and Co$_3$O$_4$ have been widely investigated for their pseudo capacitance performances in KOH aqueous electrolyte solution [7-9]. By comparison, Co$_3$O$_4$ has a high theoretical specific capacitance (3650 F/g), low toxicity and great redox ability [10]. Different methods were applied to synthesize oxide Co$_3$O$_4$, such as thermal decomposition of solid phase, chemical spray pyrolysis, chemical vapor deposition and traditional sol-gel method [11-15]. However, the size distribution of Co$_3$O$_4$ nanocrystal made by the
above methods is wide. Hydrothermal synthesis is an efficient technique for preparing fine powders by chemical reaction with high temperature and high pressure in solution [16].

In this present work, Co$_3$O$_4$ nanoparticles were prepared by hydrothermal method at different temperatures. The main point is to explore how temperatures have an influence on the crystal structures and electrochemical performance of cobalt oxide. In the experiment, we chose 140°C and 200°C as hydrothermal temperatures, and 350°C and 450°C as annealing temperatures. The crystal structures of prepared Co$_3$O$_4$ nanoparticles were characterized by TEM, XRD, XPS and N$_2$ adsorption-desorption. The capacitance performances were studied by CVs, EIS and GCD.

2. Experimental

2.1. Synthesis of Co$_3$O$_4$ nanoparticles

All of the chemicals were of analytical grade and used without further management, which were got from Alfa Assar (China). 0.03 M Co (NO$_3$)$_2$ 6H$_2$O and 0.26 M CO (NH$_2$)$_2$ were dissolved in 210 ml distilled water. The mixture was stirred by magnetic stirring apparatus until a transparent solution was obtained and then was transferred to two Teflon-lined stainless steel autoclaves (100 ml capacity) evenly. The autoclaves were filled with distilled water up to 80% of the total capacity, which were then sealed and heated at 140°C and 200°C for 3h respectively, marked as A and B. After the autoclaves were cooled down to room temperature in air naturally, the precipitate was collected and washed with distilled water and absolute ethanol 3 times in turn by centrifugation (5000 r/min). The precursor was dried in a vacuum oven at 80°C for 8h. Finally, the powder A was annealed at 350°C and 450°C respectively, and the powder B was annealed at 450°C for 2h in the air with a slow heating rate of 4°C per minute to obtain the desired Co$_3$O$_4$ nanoparticles. The three samples were marked as 140 °C - 350 °C, 140 °C - 450 °C, 200 °C - 450 °C.

2.2. Materials characterization

The morphology and nanostructure were characterized using transmission electron microscopy (TEM, Tecnai G2 F20 S-TWIN, operated at 200kV). The Brunner-Emmet-Teller (BET) surface area was measured by nitrogen adsorption-desorption. The total pore volume and mean pore size were calculated by the Barrett-Joyner-Halenda (BHJ) method. The crystal structures were studied using Analytical Pert PRO X-ray diffraction. The surface elemental analysis was performed using an X-ray photoelectron spectrometer (XPS, Thermos ESCALAB 250XI). The mass of the electroactive materials was weighed with a microbalance (Mettle Toledo) with an accuracy of 0.01 mg.

2.3. Electrochemical measurements

To measure the electrochemical performance, electrodes were fabricated by the mixture of active materials, acetylene black and polyvinylidene fluoride (PVDF) in a weight ratio of 8:1:1 with N-methylpyrrolidone (NMP). In this experiment, the mass of active material is 20 mg in each electrode. Then the slurry was evenly pressed onto the nickel foam (10×10 mm$^2$), which was used as working electrodes. The working electrode was dried at 60°C for 6h and then pressed under 6MPa for 1 min. Platinum foil was used as counter and saturated calomel electrode (SCE) as reference electrode. The electrolyte is 6M KOH aqueous solution. Cyclic volammograms (CVs) were measured using IviumStat electrochemical workstation between -0.2V and 0.5V. The electrochemical impedance spectroscopy (EIS) and Galvano static charge/discharge were measured in the electrochemical workstation (Auto lab PTN320N). The frequency of EIS ranged from 0.01Hz to 100 KHz at the open circuit potential. Charge/discharge cycles of the sample were measured between 0.01V to 0.35V at different current densities. All electrochemical measurements were carried out at room temperature.
3. Results and discussion

3.1. Characterization of materials
The XRD patterns of the products in Fig.1 show clear diffraction peaks were well indexed to (220), (311), (222), (400), (422), (511) and (440) planes of crystalline cubic Co$_3$O$_4$ (JCPDF card no. 01-074-1657; space group: Fd-3m), respectively. No obvious diffraction peaks of other impurity phases were checked out, indicating the successful preparation of pure Co$_3$O$_4$ by this hydrothermal method. Based on the highest diffraction peak (311 crystal plane), the average crystallite size of these samples are 20.2 nm, 26.9 nm and 156.9 nm from up to down in the XRD patterns, which were calculated by the Scherer formula[17]. Furthermore, as either the hydrothermal temperature or annealing temperature increased, the diffraction peak intensity was enhanced and the peak width was decreased, which mean the crystalline of Co$_3$O$_4$ nanoparticles become well. As shown in the figure, the crystallinity of 140 °C-350 °C is relatively lower.

![Figure 1. XRD patterns of Co$_3$O$_4$ nanoparticles at different temperature](image)

![Figure 2. TEM images and HRTEM images of Co$_3$O$_4$ nanoparticles (a), (d) 140°C-350°C (b), (e) 140°C-450°C (c), (f) 200°C-450°C](image)

The typical TEM and HRTEM images of different Co$_3$O$_4$ nanoparticles are displayed in the Fig.2. The TEM images (a), (b), (c) clearly demonstrate the diameter of gains become bigger as the temperature increased, which are about 10nm, 30nm and 50nm respectively in sequence. From HRTEM images (d), (e), (f), the lattice fringes with a spacing distance of 0.278nm, 0.285nm and 0.290nm are associated to the (220) crystal planes of Co$_3$O$_4$ nanoparticles. The corresponding selected area electron diffraction (SAED) pattern inset in the images (b), (d), (f) demonstrates that the oxide is
Co₃O₄ phase and the diffraction rings are mainly indexed as (440), (422), (311) and (220) respectively, which are consistent with results obtained from XRD analysis. The shorter spacing distance is beneficial for fast diffusion of the redox phase, which makes the composites display a high electrochemical capacitance [18].

To further investigate the chemical composition of these samples, X-ray photoelectron spectroscopy (XPS) was carried out. As shown in Fig. 3.(a), (b), (c), the Co 2p spectrum indicate a low energy and a high energy band at 779.9 eV and 795.3 eV, corresponding to Co 2p₁/₂ and Co 2p₃/₂, with two satellites at 788.8 eV and 805.2 eV, and these are the characteristic of Co₃O₄ phases [19]. The Co 2p₃/₂ peak of 779.9 eV can be further disassembled into two fitting peaks at 779.7 eV and 780.7 eV, and the Co 2p₁/₂ peak of 795.3 eV can be further disassembled into two fitting peaks at 794.8 eV and 796.1 eV. The peaks with the binding energy of 779.9 eV and 794.8 eV can be appointed to Co³⁺, while the peaks at 780.7 eV and 796.1 eV can be appointed to Co²⁺. As the temperature increased, the area ratio of trivalent cobalt against bivalent cobalt on the surface is 35.1%, 25.8% and 27.68%, indicating bivalent cobalt was predominant and some trivalent cobalt was transformed to bivalent cobalt. Furthermore, the high-resolution O 1s spectrum in Fig. 3 (d), (f), (e) can be further disassembled into two fitting peaks at 530.0 eV and 531.4 eV, confirming the presence of lattice oxygen and surface oxygen on the surface[20].

![XPS spectra of Co 2p of the Co₃O₄ nanoparticles and O 1s of the Co₃O₄ nanoparticles](image)

**Figure 3.** XPS spectra of Co 2p of the Co₃O₄ nanoparticles and O 1s of the Co₃O₄ nanoparticles (a), (d)140°C-350°C (b), (f) 140°C-450°C (c), (e) 200°C-450°C

The BET surface area obtained from five-point BET method is 68.142 m²/g, 24.248 m²/g, 21.516 m²/g in turn. The value of 140°C-350°C is relatively higher than another two values and most of the values reported earlier in literature (31.3 m²/g, 43.9 m²/g, 59 m²/g) [18, 21]. The pore size (diameter) distribution calculated from the Barrett-Joyner-Halenda (BJH) method shows average size pore of 2.455 nm, 2.187 nm and 2.189 nm successively in Co₃O₄ nanoparticles. Similarly, the value of 140°C-350°C Co₃O₄ nanoparticles is bigger relatively. Comparing with annealing temperature, hydrothermal temperatures have a greater influence on the BET surface area, total pore volume and mean pore size. Big pore volumes will provide short diffusion paths for electrons and ions and high surface areas can provide more active sites, which further promote electrochemical reactions. These features can particularly improve pseudo capacitive performance.
Table 1. The BET surface area, total pore volume and mean pore size of these samples

| Sample       | SBET (m²/g) | VT (cm³/g) | Mean pore size (nm) |
|--------------|-------------|------------|---------------------|
| 140°C-350°C  | 68.142      | 0.0288     | 2.455               |
| 140°C-450°C  | 24.248      | 0.009      | 2.187               |
| 200°C-450°C  | 21.516      | 0.008      | 2.189               |

3.2. Electrochemical characteristic of Co₃O₄ nanoparticles

A three-electrode installation was applied to examine the pseudo capacitive performances of these Co₃O₄ nanoparticles for supercapacitor electrode in 6 M KOH. Fig.4a shows the cyclic voltammograms (CVs) of 140°C-350°C Co₃O₄ at different scan rates with a potential window from -0.2 V to 0.5 V (vs. SCE). Two major redox peaks appeared in all CV curves, indicating the capacitance characteristic was mainly governed by pseudo capacitive reactions. With increasing sweep rates, the integrated CV area of 140°C-350°C Co₃O₄ electrode gradually increased, accompanied with redox peaks moving to more positive and negative potentials. However, the peak shape of CV curves was not deformed in any degree even though the scan rate was as high as 50mV/s, indicating the high electrochemical reversibility of the material [22].

Fig.4b shows CV curves of Co₃O₄ nanoparticles at different temperature with the scan rate of 5 mV/s. Two pairs of redox peaks showed up in CV curves. In the redox process, two sequential reactions take place as follows [23]:

\[
\text{Co}_3\text{O}_4 + \text{OH}^- + \text{H}_2\text{O} \rightleftharpoons 3\text{CoOOH} + \text{e}^- \quad (1)
\]

\[
\text{CoOOH} + \text{OH}^- \rightleftharpoons \text{CoO}_2 + \text{H}_2\text{O} + \text{e}^- \quad (2)
\]

Evidently, the area of the curve of 140°C-350°C Co₃O₄ electrode is larger than these of 140°C-450°C Co₃O₄ electrode and 200°C-450°C Co₃O₄ electrode, suggesting the 140°C-350°C Co₃O₄ electrode presents better capacitive properties on comparing with two other electrodes. The specific capacitance can be calculated using the CVs curves as follows [24]:

\[
C_m = \frac{\int_0^V Idv}{nmv} \quad (3)
\]

Where Cm (F/g) is the specific capacitance of the electrode, I (A) is the discharge current, V (V) is the potential, v (mV/s) is the scan rate, and m (g) is the mass of the electroactive materials in the electrodes. Fig.4c shows the specific capacitance of these samples at different scan rates. The specific capacitance decreased with the increase of scan rate. This behavior was due to the fact that the high scan rate can restrict the ion to all the pore of electrode [25, 26]. In the literature [27], it reported that only outer surface of Co₃O₄ nanoparticles can be used to storage charges. Specific capacitance of 140°C-350°C Co₃O₄ nanoparticles is 222, 206, 203, 160, 116 and 76 F/g at the scan rate of 5, 10, 20, 50, 100 and 200 mV/s, which is higher than those of anther Co₃O₄ nanoparticles at all the same scan rates. The result is good consistent with speculation at BET results, manifesting the 140°C-350°C Co₃O₄ electrode presents better capacitive properties in comparison with two other electrodes again.

Fig.4d compares the Galvano static charge/discharge curves for these various Co₃O₄ nanoparticles at the same current density of 0.01A/s. The obtained curves with fairly a triangular shape did not show a double-layer capacitor rather pseudo capacitance behaviors, which inferred the characteristic of charge storage mechanism [28]. Meanwhile, the charge and discharge times of 140°C-450°C Co₃O₄
nanoparticles and 200°C-450°C Co₃O₄ nanoparticles are shorter than that of 140°C-350°C Co₃O₄ nanoparticles evidently. According to the equation as follows [29]:

$$C_m = \frac{I_{ct}}{\Delta V \times m}$$

(4)

where Cm (F/g) is the specific capacitance of the electrode, I (A) is the discharge current, \(\Delta V\) (V) is the window potential, m (g) is the mass of the electroactive materials in the electrodes, the specific capacitance of 140°C-350°C Co₃O₄ nanoparticles is relatively larger than these of two other samples. Meanwhile, regarding discharge curves, IR drops of 140°C-350°C Co₃O₄ nanoparticles (0.0117 Ω) is relatively shorter than these of 140°C-450°C Co₃O₄ nanoparticles (0.0143Ω) and 140°C-350°C Co₃O₄ nanoparticles (0.0131Ω), suggesting a relatively smaller internal resistance of 140°C-350°C Co₃O₄ nanoparticles. We speculate that the high specific capacitance is due to relatively low resistance derived from the shorter crystal spacing distance. EIS was carried out to further evaluate the specific capacitance of these Co₃O₄.

![Figure 4](image-url)

**Figure 4.** (a)CV curves of 140°C-350°C Co₃O₄ at different temperatures with the scan rate of 5, 10, 20 and 50 mV/s. (b) CV curves of Co₃O₄ at different temperatures with the scan rate of 5 mV/s. (c) Plots of the specific capacitance against the scan rates. (d) The charge and discharge curves of different Co₃O₄ at a constant current density of 10mA/s. (e) Nyquist plots of different Co₃O₄ before cyclic voltammograms. (f) The enlarged part of (e)

The Nyquist curves of the obtained Co₃O₄ nanoparticles exhibit a semi-circle in the high frequency region, a straight line in the low frequency region, and a short Warburg section between the semi-circle and the slope of the line in the Fig.4e. The semi-circle in the high frequency region on the real axis represents the charge-transfer resistance, which demonstrates the electrolyte ions to the electroactive materials and the conductivity of the electrodes. The straight line ascends at the frequency region at an angle of almost 45° exhibits Warburg resistance" indicating the ion diffusion resistance of the charged ions of Co₃O₄. The straight line in the low frequency region displays the ideal capacitance behavior nature [30, 31]. The 140°C-350°C Co₃O₄ nanoparticles has a smaller charge-transfer resistance value in the high frequency region and a more vertical line in the low
frequency region than another two Co$_3$O$_4$, suggesting the 140°C-350°C Co$_3$O$_4$ nanoparticles has a better capacitive behavior. The result is in great corresponding to the previous sections in the IR drops and gives an explanation for the higher specific capacitance of the 140°C-350°C Co$_3$O$_4$ nanoparticles.

Above all, the 140°C-350°C Co$_3$O$_4$ nanoparticles have a better capacitive behavior, which can be explained in terms with shorter crystal spacing distance, larger BET surface area and more bivalent cobalt on the surface.

4. Conclusion
In summary, Co$_3$O$_4$ was prepared by hydrothermal method at different temperatures successfully. The morphology, surface area, crystal structures and surface elemental analysis were studied in detail with the support of TEM, N$_2$ adsorption-desorption, XRD and XPS in sequence. The 140°C-350°C Co$_3$O$_4$ has a shorter crystal spacing distance indexed to the (220) crystal planes, larger BET surface area and more bivalent cobalt on the surface. In addition, the 140°C-350°C Co$_3$O$_4$ exhibits excellent pseudo capacitance behavior. The specific capacitance of it was higher in comparing with 140°C-450°C Co$_3$O$_4$ and 200°C-450°C Co$_3$O$_4$ in 6 M KOH aqueous solution according to the results of cyclic voltammograms (CVs), electrochemical impedance spectroscopy (EIS) and Galvano static charge/discharge, which was in good agreement with their crystal structure. Due to low hydrothermal temperature and annealing temperature of 140°C-350°C Co$_3$O$_4$, it can be relatively low cost to be benefit of a potential electrode for supercapacitor application.

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References
[1] G. Wang, L. Zhang, J. Zhang, A review of electrode materials for electrochemical supercapacitors, Chem. Soc. Rev. 41(2012) 797-828.
[2] H. Wang, H. Dai, Strongly coupled inorganic-nano-carbon hybrid materials for energy storage, Chem. Soc. Rev. 42 (2013) 3088-3113.
[3] Y. Luo, J. Jiang, W. Zhou, H. Yang, X. Qi, H. Zhang, H. J. Fan, D. Y. W. Yu, C. M. Li, T. Yu, Seed-assisted synthesis of highly ordered TiO$_2$@α-Fe$_2$O$_3$ core/shell arrays on carbon textiles for lithium-ion battery applications, Energy. Environ. Sci. 5(2012) 6559-6566.
[4] C. Liu, F. Li, L.P. Ma, H.M. Cheng, Advanced materials for energy storage, Adv. Mater. 22 (2010) E28–E62.
[5] Z. Chen, Y. Qin, D. Weng, Q. Xiao, Y. Peng, X. Wang, H. Li, F. Wei, Y. Lu, Design and synthesis of hierarchical nanowire composites for electrochemical energy storage, Adv. Funct. Mater. 19 (2009) 3420–3426.
[6] A. Manthiram, A. Vadivel Murugan, A. Sarkar, T. Muraliganth, Nanostructured electrode materials for electrochemical energy storage and conversion, Energy Environ. Sci. 1 (2008) 621–638.
[7] F. Shi, L. Li, X. L. Wang, C. D. Gu, J. P. Tu, Metal oxide/hydroxide-based materials for supercapacitors, RSC Adv 2014; 4: 41910–21.
[8] H. Jiang, J. Ma, C. Li, Mesoporous carbon incorporated metal oxide nanomaterials as supercapacitor electrodes. Adv Mater 2012; 24: 4197–202.
[9] M. Zhi, C. Xiang, J. Li, M. Li, N. Wu, Nanostructured carbon–metal oxide composite electrodes for supercapacitors: a review. Nanoscale 2013; 5: 72–88.
[10] M. Deng, F. Huang, I. Sun, W.T. Tsai, J. Chang, An entirely electrochemical preparation of a nano-structured cobalt oxide electrode with superior redox activity, Nanotechnology 20 (2009) 175602.
[11] M. R. Tarasevich, B. N. Efremov, Electrodes of Conductive Metallic Oxides, Part A, Elsevier,
Amsterdam, 1980, Chapter 5;

[12] R.N. Singh, J.F. Koenig, G. Poillerat, P.J. Chartier, Electrochem. Soc.137 (1990) 1480;
[13] M. Hamdani, J.F. Koenig, P.J. Chartier, Appl. Electrochem. 18 (1988) 568;
[14] C.S. Cheng, M. Serizawa, H. Sakata, T. Hirayama, Mater. Chem. Phys. 53 (1998) 255;
[15] M.E. Baydi, G. Poillerat, J.L. Rehspringer, J.L. Gautier, J.F. Koenig, P.J. Chartier, Solid State Chem 109 (1994) 281.
[16] L.J. Cote, A.S. Teja, A.P. Wilkinson, Z.J. Zhang, Continuous hydrothermal synthesis and crystallization of magnetic oxide nanoparticles [J]. J Mater Res, 2002, 17(9): 2410-2416.
[17] H.P. Klug, L.E. Alexander, X-ray Diffraction Procedures: for Polycrystalline and Amorphous Materials, second ed., Wiley, New York, 1974.
[18] J.L. Lv, W.L. Guo, T.X. Liang, Synthesis of Co3O4@CoMoO4 core–shell architectures nanocomposites as high-performance supercapacitor electrode, Journal of Electroanalytical Chemistry 783 (2016) 250–257
[19] X. Xiang, L. Zhang, H.I. Him, F. Li, D.G. Evans, Co-based catalysts from Co/Fe/Al ayered double hydroxides for preparation of carbon nanotubes, Appl. Clay Sci.42 (2009) 405–409.
[20] J.C. Dupin, D. Gonbeau, I. Martin-Litas, P. Vinatier, A. Levasseur, Lithium intercalation/deintercalation in transition metal oxides investigated by X-ray photoelectron spectroscopy, J. Electron Spectrosc. Relat. Phenom. 120 (2001)55–65
[21] D. Feng, X.Q. Zuo, Q. Yang, G. Li, Z.L. Ding, M.Z. Wu, Y.Q. M , S.W. Jin, K.R. Zhu, Facile hydrothermal reduction synthesis of porous Co3O4 nanosheets@RGO nanocomposite and applied as a supercapacitor electrode with enhanced specific capacitance and excellent cycle stability, Electrochimica Acta 222 (2016) 976–982.
[22] J. W. Lee, T. Ahn, J. H. Kim, J. M. Ko, J. D. Kim, Nanosheets based mesoporous NiO microspherical structures via facile and template-free method for high performance supercapacitors, Electrochim. Acta 56 (2011) 4849–4857.
[23] W. Liu, X. Li, M. Zhu, X. He, High-performance all-solid state asymmetric supercapacitor based on Co3O4 nanowires and carbon aerogel, J. Power Sources 282 (2015) 179–186
[24] Adhikari MP, Adhikari R, Shrestha RG, Rajendran R, Adhikari L, Bairi P, et al. Nanoporous activated carbons derived from agro-waste corncob for enhanced electrochemical and sensing performance, Bull Chem Soc Jpn 2015;88:1108–15.
[25] R.B. Rakhi, W. Chen, D. Cha, H.N. Alshareef, Substrate dependent selforganization of mesoporous cobalt oxide nanowires with remarkable pseudocapacitance, Nano Lett. 12 (2012) 2559–2567.
[26] D. S. Achilleos, T. A. Hatton, Surface design and engineering of hierarchical hybrid nanostructures for asymmetric supercapacitors with improved electrochemical performance, J. Colloid Interf. Sci. 447 (2015) 282–301.
[27] K.Y. Zhang, H. Chen, X. Wang, D.L. Guo, C.G. Hu, S.X. Wang, J.L. Sun, Q. Leng, Synthesis and structure determination of potassium copper selenide nanowires and solid-state supercapacitor application, J. Electrode Sources 268 (2014) 522–532.
[28] G.S. Gund, D.P. Dubalb, B.H. Patil, S.S. Shinde, C.D. Lokhande, Enhanced activity of chemically synthesized hybrid graphene oxide/Mn3O4 composite for high performance supercapacitors, Electrochim. Acta 92 (2013) 205–215
[29] Gopalkrishnan M, Srikesh G, Mohan A, Arivazhagan V, In-situ synthesis of Co3O4/graphite nanocomposite for high-performance supercapacitor electrode applications, Applied Surface Science 403 (2017) 578–583.
[30] P. L. Taberna, P. Simon, J. F. Fauvarque, Electrochemical characteristics and impedance spectroscopy studies of carbon/carbon supercapacitor, J.Electrochem. Soc. 150 (2003) A292–300
[31] Y. Wang, Z. Shi, Y. Q. Huang, Y. F. Ma, C. Y. Wang, M. M. Chen, Y. Y. Chen, Supercapacitor devices based on graphene materials, J. Phys. Chem. C113 (2009) 13103–13107.