UNIVERSITI PUTRA MALAYSIA

INCORPORATION OF METAL OXIDES IN ELECTROPOLYMERIZATION OF POLY(3,4-ETHYLENEDIOXYTHIOPHENE)/GRAPHENE OXIDE FOR SUPERCAPACITOR

NUR HAWA NABILAH BINTI AZMAN

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By

NUR HAWA NABILAH BINTI AZMAN

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Doctor of Philosophy

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Chairman: Associate Professor Yusran Sulaiman, PhD
Faculty: Science

Supercapacitor is a type of energy storage device which is useful for storing a large amount of energy that can be charged and discharged in short amount of time with long life span. Electrode material which is the most important part of supercapacitor plays an important role in storing a high amount of energy. In this study, composites consisting of poly(3,4-ethylenedioxythiophene) (PEDOT), graphene oxide (GO) and metal oxides were prepared and its supercapacitive performances as electrode materials for supercapacitor were studied. Initially, different applied potentials, concentration of GO and electropolymerization times were studied for the preparation of PEDOT/GO. It was revealed that PEDOT/GO with 1 mg/ml GO electropolymerized for 10 minutes at 1.2 V exhibited the highest specific capacitance. In order to further improve the supercapacitive performance of the composite, metal oxides (MnO_2, Fe_2O_3 and MnO_2/Fe_2O_3) which are recognized for their high specific capacitance were introduced into the optimized PEDOT/GO composite. Various concentrations and the molar ratio of metal oxides precursor were studied to prepare PEDOT/GO/MnO_2, PEDOT/GO/Fe_2O_3 and PEDOT/GO/MnO_2/Fe_2O_3.

Raman spectroscopy and Fourier transform infrared (FTIR) spectra revealed the composites were successfully incorporated with metal oxides upon the addition of MnO_2, Fe_2O_3 and MnO_2/Fe_2O_3 into PEDOT/GO. The presence of metal oxides in the PEDOT/GO was further confirmed via X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) measurements and the results displayed all the distinctive peaks of MnO_2, Fe_2O_3 and MnO_2/Fe_2O_3. In

addition, from the XRD and XPS, the phases of the metal oxides were also confirmed as MnO_2 and Fe_2O_3 (hematite) with oxidation states of Mn^{4+} and Fe^{3+}, respectively. The supercapacitive properties of the composites were studied by sandwiching two electrodes together and separated by a filter paper soaked in 1 M KCl. PEDOT/GO/MnO_2/Fe_2O_3 composite exhibited the highest specific capacitance (287 F/g) compared to PEDOT/GO/MnO_2 (239 F/g), PEDOT/GO/Fe_2O_3 (221 F/g) and PEDOT/GO (73 F/g) at 25 mV/s. The MnO_2 and Fe_2O_3 particles were successfully anchored on the wrinkled paper-like sheets of PEDOT/GO as can be seen from FESEM images which acted as spacers in order to improve the supercapacitive performances by maximizing the utilization of electrode materials by the electrolyte ions. The PEDOT/GO/MnO_2/Fe_2O_3 is a suitable candidate for a high-performance supercapacitor due to the synergistic effect provided by the PEDOT, GO, MnO_2 and Fe_2O_3 that help to enhance the performance of the composite for supercapacitor application as revealed from GCD with specific energy and power of 11 Wh/kg and 1900 W/kg at 4 A/g, respectively. The PEDOT/GO/MnO_2/Fe_2O_3 composite also revealed the lowest charge transfer resistance that leads to the superior supercapacitive performances. Thus, PEDOT/GO/MnO_2/Fe_2O_3 composite displayed the highest supercapactive performances compared to PEDOT/GO/MnO_2 and PEDOT/GO/Fe_2O_3.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

PENGGABUNGAN LOGAM OKSIDA KE DALAM POLIMER (3,4-ETILDIOKSITIOFENA)/GRAFEN OKSIDA UNTUK SUPERKAPASITOR

Oleh

NUR HAWA NABILAH BINTI AZMAN

April 2018

Pengerusi: Prof Madya Yusran Sulaiman, PhD
Fakulti: Sains

Superkapasitor adalah sejenis alat penyimpan tenaga yang amat berguna untuk menyimpan tenaga dalam jumlah besar dan boleh dicaj dan discaj dalam jangka masa yang pendek serta mempunyai jangka hayat yang panjang. Bahan elektrod merupakan bahagian superkapasitor yang paling penting dalam memainkan peranan sebagai penyimpan tenaga yang besar. Oleh itu, di dalam penyelidikan ini, komposit terdiri daripada polimer (3,4-etildioksitiofena) (PEDOT), grafen oksida (GO) dan logam oksida disediakan dan prestasi superkapasitif komposit tersebut sebagai bahan elektrod untuk superkapasitor dikaji. Permulannya, kesan keupayaan, kepekatan GO dan masa pempolimeran elektrokimia telah dikaji untuk menghasilkan PEDOT/GO. PEDOT/GO dengan kepekatan 1 mg/ml GO dielektropolimerkan selama 10 minit pada voltan 1.2 V menghasilkan kapasitan spesifik yang paling tinggi. Demi meningkatkan prestasi superkapasitor komposit, logam oksida (MnO_2, Fe_2O_3 and MnO_2/Fe_2O_3) yang terkenal dengan prestasi kapasitan spesifik yang tinggi telah diperkenalkan di dalam komposit optimum PEDOT/GO. Pelabagai kepekatan dan nisbah kepekatan telah dikaji untuk menghasilkan PEDOT/GO/MnO_2, PEDOT/GO/Fe_2O_3 dan PEDOT/GO/MnO_2/Fe_2O_3.

Spektroskopi Raman dan spektroskopi Fourier inframerah (FTIR) telah menunjukkan bahawa semua komposit tersebut telah berjaya digabungkan dengan logam oksida selepas penambahan MnO_2, Fe_2O_3 dan MnO_2/Fe_2O_3 ke dalam PEDOT/GO. Kehadiran logam oksida juga disahkan menggunakan belauan sinar-x (XRD) serta spektroskopi fotoelektron sinar-x (XPS) dan hasil

kajian menunjukkan semua puncak tersendiri logam oksida MnO_2, Fe_2O_3 dan MnO_2/Fe_2O_3 hadir di dalam komposit tersebut. Sebagai tambahan, hasil kajian XRD dan XPS juga menunjukkan bahawa fasa logam oksida MnO_2 dan Fe_2O_3 (hematit) masing-masing sebagai Mn^{4+} and Fe^{3+}. Ciri-ciri superkapasitif komposit tersebut dikaji dengan menggabungkan dua elektrod yang sama dan dipisahkan oleh kertas turas direndam dalam 1 M KCl. Komposit PEDOT/GO/MnO_2/Fe_2O_3 menghasilkan nilai kapasitan spesifik paling tinggi (287 F/g) berbanding PEDOT/GO/MnO_2 (239 F/g), PEDOT/GO/Fe_2O_3 (221 F/g) dan PEDOT/GO (73 F/g) pada kadar imbas 25 mV/s. Partikel MnO_2 dan Fe_2O_3 dilihat berjaya menyauh pada kepingan PEDOT/GO berkedut seperti yang dapat dilihat dalam imej FESEM serta bertindak sebagai penjarak untuk meningkatkan prestasi superkapasitif dengan memaksimumkan penggunaan bahan elektrod oleh ion elektrolit. PEDOT/GO/MnO_2/Fe_2O_3 adalah calon sesuai untuk superkapasitor berprestasi tinggi kerana kesan sinegistik yang disediakan oleh PEDOT, GO, MnO_2 dan Fe_2O_3 membantu dalam meningkatkan prestasi komposit seperti yang ditunjukkan oleh GCD dengan nilai tenaga dan kuasa spesifik masing-masing 11 Wh/kg dan 1900 W/kg pada 4 A/g. Komposit PEDOT/GO/MnO_2/Fe_2O_3 juga ditunjukkan mempunyai nilai rintangan permindahan caj, R_{ct} terendah yang membawa kepada ciri-ciri superkapasitif unggul. Maka, komposit PEDOT/GO/MnO_2/Fe_2O_3 mempunyai ciri-ciri superkapasitif yang paling unggul berbanding komposit PEDOT/GO/MnO_2 dan PEDOT/GO/Fe_2O_3.

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I certify that a Thesis Examination Committee has met on 24th April 2018 to conduct the final examination of Nur Hawa Nabilah Binti Azman on her thesis entitled "Incorporation of metal oxides (Metal = Manganese and Iron) in the electropolymerizeation of poly(3,4-ethylenedioxythiophene)/graphene oxide for supercapacitor" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the degree Doctor of Philosophy.

Members of the Thesis Examination Committee were as follows:

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

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LIST OF SYMBOLS

Symbol	Meaning	Usual unit
I	Current applied	A
C_{sp}	Specific capacitance	F/g
E	Specific energy	Wh/kg
P	Specific power	W/kg
V	Voltage	V
ΔV	Potential window	V
Δt	Discharging time	s
R_{ct}	Charge transfer resistance	Ω
ESR	Equivalent series resistance	Ω
u	Scan rate	V/s
χ^2	Chi square	-
Z'	Real impedance	Ω
Z''	Imaginary impedance	Ω

LIST OF ABBREVIATIONS

AC	alternating current
Ag/AgCl	silver/silver chloride
AuNPs	Au nanoparticles
CB	carbon black
C_{dl}	double layer capacitor
CF	carbon fiber
CNF	carbon nanofibril
CNT	carbon nanotubes
CP	conducting polymer
CPE	constant phase element
CSS	commercial supercapacitor separator
CV	Cyclic voltammetry
CVs	cyclic voltammograms
EDLC	electrical double layer capacitors
EDOT	3, 4-ethylenedioxythiophene
EIS	electrochemical impedance spectroscopy
FESEM	Field emission scanning electron microscopy
FTIR	Fourier transforms infrared spectroscopy
GCD	galvanostatic charge-discharge
GO	graphene oxide
ITO	indium tin oxide
lCNT	long carbon nanotubes

LED	light emitting diode
MWCNTs	multi walled carbon nanotubes
NapTS	sodium p-toluenesulfonate
OCP	open circuit potential
PANI	polyaniline
PEDOT	poly (3,4-ethylenedioxythiophene)
PEDOT:PSS	poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate)
PPy	polypyrrole
PVA/H_3PO_4	polyvinyl alcohol/phosphoric acid
RGO	reduced graphene oxide
SCE	Standard calomel electrode
sCNT	short carbon nanotubes
s-G/PPy	sulfonated grapheme/polypyrrole
SHE	Standard hydrogen electrode
SS	stainless steel
T	hyperbolic tangent
W	Warburg
XPS	X-ray photoelectron spectrometer
XRD	X-ray diffraction diffractometer

CHAPTER 1

INTRODUCTION

1.1 Background of research

Energy can exist in various forms such as heat energy, electrical energy, nuclear energy and gravitational energy. There are two types of energy sources i.e. renewable and non- renewable. Non-renewable energy is produced from fossil fuels such as petroleum, natural gas and coal which cannot be replenished. Fossil fuels are formed hundreds of millions years ago from decayed planktons, algae and plants under the seabed. During their lives, these planktons, algae and plants accumulate energy through a process called photosynthesis in which light energy i.e. sunlight is converted into chemical energy. This chemical energy which is trapped in the planktons, algae and plants can be exploited when they are burnt. The sediments and rocks which piled up on top of them cause pressure and high heat underground and eventually turn them into fossil fuels.

Fossil fuels are precious source of energy and have been used as the main source of energy worldwide in order to generate electricity. However, these fossil fuels cannot last long because eventually, it will deplete as it cannot be restored in short amount of time. In addition, the burning of the fossil fuels contributes to global warming due to the increasing of carbon dioxide (CO_2) in the atmosphere. Global warming causes the rises of climate temperature and affect human health and environment. In the Earth's poles, the ice glaciers begin to melt and contribute to the rise of sea level. Besides, global warming gives impact on many species that inhabit the poles such as penguins and polar bears. They are becoming endangered species due to the ice melting. As for human health, global warming triggers the spread of transmitted diseases such as malaria and diarrhea as a result of droughts and floods. Thus, in order to prevent global warming and depletion of fossil fuels, renewable energy is needed.

Renewable energy is a type of energy that is produced from renewable sources such as wind, solar, biomass and geothermal heat (Bundhoo, 2018). Wind is used to operate wind turbines in order to generate electricity and it is widely applied in a few of countries such as the USA, Canada and China. Solar energy which captured energy from sunlight is mainly used to harvest electrical energy. Biomass can be converted into biofuel and methane gas to be

consumed for transportation whereas geothermal energy can be used to generate electricity from the geothermal heat stored in the earth crust. Renewable energy is always preferable due to its low CO_2 emission compared to fossil fuels (Holma *et al.*, 2018) and the energy source is everlasting. Thus, utilization of renewable energy sources can help to decrease the environmental pollution and reliance on fossil fuels petroleum and gas which are becoming hard to discovered and costly. As a result of attentiveness of renewable energy, efficient energy storage technology is demanded to sustain the supply of energy.

Consumption of energy increases gradually due to the growth of the economy and the human population worldwide. According to United Nation, the human population worldwide is almost 7.6 billion in mid-2017 through the *2017 Revision of World Population Prospects*. It is estimated that every year 83 million people are added to the world human population and the numbers will increase to 8.6 billion in 2030 and 11.2 billion in 2100. Therefore, it is important to sustain the renewable energy in order to meet the demand of energy consumption in our daily lives. Every day, energy is used for residential use such as watching television, lighting the lights and charging phones. Besides, energy is also used for transportation and commercial use in order to operate a business such as computers and workstations. Hence, in order to meet the energy demand in our daily lives, development of renewable and sustainable energy is crucial.

There are numerous technologies of energy storage systems that have been developed over past few decades such as supercapacitor and battery. In comparison to the battery, supercapacitor has gained a lot of attraction due to its ability to store large energy in short amount of time and environmental friendly as less toxic substances are used during the preparation of supercapacitor. Therefore, the supercapacitor is extensively used in wide range of applications such as hybrid electric vehicles, airbus and power systems. Hybrid electric vehicles are developed to reduce the emission of CO_2 in an effort to protect the environment and human health. Besides, the supercapacitor is also used in hybrid electric vehicles to boost acceleration and braking systems recovery (Zhong *et al.*, 2015). In Airbus, the supercapacitor is employed to open the emergency doors in case of power failures. This technology is recently used on Airbus A380 jumbo jets (Simon and Gogotsi, 2008). There is more research on supercapacitor electrode materials that can be explored for energy storage. Thus, it is essential to develop electrode materials which meet the energy demand in order to be employed in advanced technology.

1.2 Problem Statement

Supercapacitors are desirable energy storage devices due to its high specific capacitance, long operational life and high specific power. In addition, the great demand for energy consumption in daily life causes the yearning for energy risen. In order to meet these demands, high-performance electrodes for supercapacitor are needed. Electrode materials are crucial for fabricating supercapacitor with high-supercapacitive performance i.e high specific capacitance, high specific energy and power and good cycling stability. Carbon-based materials, conducting polymers and metal oxide are types of electrode materials used for supercapacitor and they are usually incorporated together to produce binary composite or even ternary composite. This is because single material electrode alone cannot achieve the quality of high-performance supercapacitor. Hence, incorporating the materials together can help to fill in each other merits and demerits.

Theoretically, metal oxides are found to produce electrodes with high specific capacitance. Among metal oxides, manganese and iron oxide are preferred due to their low-cost and less toxicity. However, metal oxides are normally suffered from low conductivity and poor cycling stability. This phenomenon limits the use of metal oxides in supercapacitor applications for long-term energy usage. In order to compensate the low conductivity of metal oxide, conducting polymers which possess high conductivity will be introduced. PEDOT is a type of conducting polymer known for its high conductivity and high chemical stability. Nevertheless, PEDOT is well known for its limited cycling stability similar to metal oxides. Thus, carbon-based materials such as graphene oxide which is recognized for its high cycling stability are introduced to improve the life cycle of the composite. In addition, the high surface area of graphene oxide can also help to provide more capacity for energy storage.

Thus, a facile preparation of PEDOT/GO with different metal oxides (MnO_2, Fe_2O_3 and MnO_2/Fe_2O_3) are introduced to improve the supercapacitive performance of the composites. Based on the advantages and disadvantages of each material mentioned above, the synergistic effect of the materials i.e. metal oxides (MnO_2, Fe_2O_3 and MnO_2/Fe_2O_3) graphene oxide and PEDOT can help to improve the specific capacitance, energy density and stability in charge discharging cycling of the composites in comparison to binary composite (PEDOT/GO) for supercapacitors applications.

1.3 Objectives

The aim of this research is to prepare and study the electrochemical performances of the electrodeposited PEDOT/GO, PEDOT/GO/MnO_2, PEDOT/GO/Fe_2O_3 and PEDOT/GO/MnO_2/Fe_2O_3 for supercapacitor. The objectives of this research are:

1. To prepare PEDOT/GO hybrid material using chronoamperometry technique and investigate the effects of concentration of GO, applied potential, electrodeposition time on PEDOT/GO composite for supercapacitor applications.
2. To prepare and evaluate the effects of concentration of manganese and iron salt on supercapacitor performance of PEDOT/GO/MnO_2 and PEDOT/GO/Fe_2O_3 for supercapacitor application.
3. To study the molar ratios of manganese and iron salt on the supercapacitive performance of PEDOT/GO/MnO_2/Fe_2O_3.
4. To compare the supercapacitive performance of PEDOT/GO, PEDOT/GO/MnO_2 PEDOT/GO/Fe_2O_3 and PEDOT/GO/MnO_2/Fe_2O_3.

1.4 Organization of chapters

Chapter 1 discusses the background of research on renewable energy, problem statement and objectives of the research. Chapter 2 reviews the fundamental of supercapacitor and the recent researches that have been done on ternary composite based on derivatives of graphene with different types of conducting polymers and metal oxide. Chapter 3 elaborates on the chemicals used and general experimental procedures. Chapter 4 describes the effect of electropolymerization parameter i.e. potential applied and electropolymerization time on the supercapacitive performance of PEDOT/GO via three-electrode configuration. Chapter 5 discuss the effect of different concentrations of GO and different electrolytes (1 M KCl, H_2SO_4, Na_2SO_4 ad KOH) on the supercapacitive performance of PEDOT/GO via two-electrode configuration. Chapter 6 elaborates the performance of PEDOT/GO after addition of manganese oxide for supercapacitor. In addition, chapter 6 explains the impact of various concentrations of manganese salt on the PEDOT/GO/MnO_2. Chapter 7 discusses the effect of different amount of iron salt incorporated into PEDOT/GO. Chapter 8 describes the supercapacitive performance of PEDOT/GO/MnO_2/Fe_2O_3 composite after addition of both manganese oxide and iron oxide and effect of the molar ratio of manganese and iron salt on PEDOT/GO/MnO_2/Fe_2O_3 composite. Chapter 9 discusses the conclusion of the research, significant of findings and recommendation for future study.

References

[1] D.P. Dubal, W.B. Kim, C.D. Lokhande, Galvanostatically deposited Fe: MnO_2 electrodes for supercapacitor application, J. Phys. Chem. Solids, 73 (2012) 18-24.

[2] K.V. Sankar, R.K. Selvan, Fabrication of flexible fiber supercapacitor using covalently grafted $CoFe_2O_4$/reduced graphene oxide/polyaniline and its electrochemical performances, Electrochim. Acta, 213 (2016) 469-481.

[3] M.T. Tung, H.T.B. Thuy, L.T.T. Hang, Metal doped manganese oxide thin films for supercapacitor application, Journal of Nanoscience and Nanotechnology, 15 (2015) 6949-6956.

[4] T. Prasankumar, V.S. Irthaza Aazem, P. Raghavan, K. Prem Ananth, S. Biradar, R. Ilangovan, S. Jose, Microwave assisted synthesis of 3D network of Mn/Zn bimetallic oxide-high performance electrodes for supercapacitors, J. Alloys Compd., 695 (2017) 2835-2843.

[5] L. Tong, K.H. Skorenko, A.C. Faucett, S.M. Boyer, J. Liu, J.M. Mativetsky, W.E. Bernier, W.E. Jones, Vapor-phase polymerization of poly(3,4-ethylenedioxythiophene) (PEDOT) on commercial carbon coated aluminum foil as enhanced electrodes for supercapacitors, J. Power Sources, 297 (2015).

[6] H. Choi, H. Yoon, Nanostructured electrode materials for electrochemical capacitor applications, Nanomaterials, 5 (2015) 906-936.

[7] F. Li, X. Jiang, J. Zhao, S. Zhang, Graphene oxide: A promising nanomaterial for energy and environmental applications, Nano Energy, 16 (2015) 488-515.

[8] Z. Zhao, G.F. Richardson, Q. Meng, S. Zhu, H.-C. Kuan, J. Ma, PEDOT-based composites as electrode materials for supercapacitors, Nanotechnology, 27 (2015) 042001.

[9] K.V. Sankar, R.K. Selvan, The ternary $MnFe_2O_4$/graphene/polyaniline hybrid composite as negative electrode for supercapacitors, J. Power Sources, 275 (2015) 399-407.

[10] G. Zhu, J. Yang, Y. Liu, X. Xie, Z. Ji, J. Yin, X. Shen, Porous Fe-Mn-O nanocomposites: Synthesis and supercapacitor electrode application, Progress in Natural Science: Materials International, 26 (2016) 264-270.

[11] N.H.N. Azman, H.N. Lim, Y. Sulaiman, Effect of electropolymerization potential on the preparation of PEDOT/graphene oxide hybrid material for supercapacitor application, Electrochim. Acta, 188 (2016) 785-792.

[12] N.H.N. Azman, H.N. Lim, Y. Sulaiman, Influence of concentration and electrodeposition time on the electrochemical supercapacitor performance of poly(3,4-ethylenedioxythiophene)/graphene oxide hybrid material, J Nanomater, 2016 (2016) 1-10.

[13] H. Zhou, H.-J. Zhai, G. Han, Superior performance of highly flexible solid-state supercapacitor based on the ternary composites of graphene oxide supported poly(3,4-ethylenedioxythiophene)-carbon nanotubes, J. Power Sources, 323 (2016) 125-133.

[14] D. Yu, J. Yao, L. Qiu, Y. Wang, X. Zhang, Y. Feng, H. Wang, In situ growth of Co_3O_4 nanoparticles on a-MnO_2 nanotubes: a new hybrid for high-performance supercapacitors, J. Mater. Chem. A, 2 (2014) 8465-8471.

[15] P. Tang, L. Han, L. Zhang, Facile Synthesis of graphite/PEDOT/MnO_2 Composites on Commercial Supercapacitor Separator Membranes as Flexible and High-Performance Supercapacitor Electrodes, ACS Appl. Mater. Interfaces, 6 (2014) 10506-10515.

[16] C. Wei, H. Pang, B. Zhang, Q. Lu, S. Liang, F. Gao, Two-Dimensional β-MnO2 Nanowire Network with Enhanced Electrochemical Capacitance, Sci. Rep., 3 (2013) 2193.

[17] Z. Ye, B. Wang, G. Liu, Y. Dong, X. Cui, X. Peng, A. Zou, D. Li, Micropore-dominant Vanadium and Iron Co-doped MnO_2 hybrid film electrodes for high-performance supercapacitors, J. Electrochem. Soc., 163 (2016) A2725-A2732.

[18] G. Nie, X. Lu, M. Chi, Y. Zhu, Z. Yang, N. Song, C. Wang, Hierarchical α-Fe_2O_3@MnO_2 core-shell nanotubes as electrode materials for high-performance supercapacitors, Electrochim. Acta, 231 (2017) 36-43.

[19] J. Chen, Y. Wang, J. Cao, Y. Liu, J.-H. Ouyang, D. Jia, Y. Zhou, Flexible and solid-state asymmetric supercapacitor based on ternary graphene/MnO_2/carbon black hybrid film with high power performance, Electrochim. Acta, 182 (2015) 861-870.

[20] W. Hui, X. Chen, X. Jing, L. Linfeng, F. Zhiyong, C. Xiaoyuan, S. Ye, L. Dongdong, Enhanced supercapacitance in anodic TiO_2 nanotube films by hydrogen plasma treatment, Nanotechnology, 24 (2013) 1-7.

[21] J. Shabani Shayeh, A. Ehsani, M.R. Ganjali, P. Norouzi, B. Jaleh, Conductive polymer/reduced graphene oxide/Au nano particles as efficient composite materials in electrochemical supercapacitors, Appl. Surf. Sci., 353 (2015) 594-599.

[22] M. Hao, Y. Chen, W. Xiong, L. Zhang, L. Wu, Y. Fu, T. Mei, J. Wang, J. Li, X. Wang, Coherent polyaniline/graphene oxides/multi-walled carbon nanotubes ternary composites for asymmetric supercapacitors, Electrochim. Acta, 191 (2016) 165-172.

[23] T. Lindfors, Z.A. Boeva, R.-M. Latonen, Electrochemical synthesis of poly(3,4-ethylenedioxythiophene) in aqueous dispersion of high porosity reduced graphene oxide, RSC Adv., 4 (2014) 25279-25286.

[24] Q. Wu, M. Chen, S. Wang, X. Zhang, L. Huan, G. Diao, Preparation of sandwich-like ternary hierarchical nanosheets manganese dioxide/polyaniline/reduced graphene oxide as electrode material for supercapacitor, Chem. Eng. J., 304 (2016) 29-38.

[25] T. Zhu, S. Zheng, Y. Lu, Y. Chen, Y. Chen, H. Guo, Influence of iron concentration and post-annealing temperature on structure and pseudocapacitive characteristics of a MnO_2-Fe_2O_3 nanocomposite, J. Solid State Electrochem., 19 (2014) 381-390.

[26] G. Han, Y. Liu, E. Kan, J. Tang, L. Zhang, H. Wang, W. Tang, Sandwich-structured MnO_2/polypyrrole/reduced graphene oxide hybrid composites for high-performance supercapacitors, RSC Adv., 4 (2014) 9898-9904.

[27] M. Li, H. He, Study on electrochemical performance of multi-wall carbon nanotubes coated by iron oxide nanoparticles as advanced electrode materials for supercapacitors, Vacuum, 143 (2017) 371-379.