



شبكة المعلومات الجامعية
التوثيق الإلكتروني والميكروفيلم

بسم الله الرحمن الرحيم



MONA MAGHRABY



شبكة المعلومات الجامعية
التوثيق الإلكتروني والميكروفيلم



شبكة المعلومات الجامعية التوثيق الإلكتروني والميكروفيلم



MONA MAGHRABY



شبكة المعلومات الجامعية
التوثيق الإلكتروني والميكروفيلم

جامعة عين شمس

التوثيق الإلكتروني والميكروفيلم

قسم

نقسم بالله العظيم أن المادة التي تم توثيقها وتسجيلها
علي هذه الأقراص المدمجة قد أعدت دون أية تغيرات



يجب أن

تحفظ هذه الأقراص المدمجة بعيدا عن الغبار



MONA MAGHRABY



Ain Shams University
Faculty of science
Chemistry department

Synthesis of nanostructures of some transition metal compounds for energy storage applications.

Thesis submitted by

Sayed Yehia Sayed Ali Attia

(M.Sc. Chemistry 2016)

*For the degree of
Doctor of philosophy [Ph.D.]
(In Chemistry)*

To

Chemistry Department

Faculty of science

Ain Shams University

2020



Ain Shams University
Faculty of science
Chemistry department

Synthesis of nanostructures of some transition metal compounds for energy storage applications.

Presented by

Sayed Yehia Sayed Ali Attia

Supervised by

Prof. Dr. Hamdi Hassanein Hassan

Professor of physical chemistry- Faculty of science-
Ain Shams University.

Prof. Dr. Yosry Fathalla Barakat

Professor of inorganic chemistry- Tabbin institute
for metallurgical studies.

Dr. Saad Gomaa Mohamed

Lecturer of physical chemistry- Tabbin
institute for metallurgical studies.

Prof. Dr. Ayman Ayoub Abdel-Shafi

Head of Chemistry Department

Abstract

In recent years, considerable research has long been devoted to the development of energy-storage devices to store the electrical energy obtained from renewable energy sources and supply the world with energy on demand. These energy-storage systems have to be more efficient and compatible with the ongoing rapid technological progress in different fields including portable electronics and electric vehicles that required both high power and high energy density. Supercapacitors, one of the most efficient electrochemical energy storage systems that attract much attention for next-generation energy storage devices that bridge the gap between the traditional capacitors (having high power density) and the batteries (having high energy density). From the merits of supercapacitors, environmental benignity, besides its unique electrochemical properties including long charge/discharge cycling life, safe operation, and high power density than batteries.

The bottleneck of supercapacitors is to increase its relatively low energy density without sacrificing its high power density and this can be done by selecting efficient electrode material concerning its electrochemical activity, conductivity, effective contact area, morphology, and porosity.

Therefore, the key aspect to enhance the performance of these kinds of energy devices is to develop and improve the performance of these active materials. In this regard, nanostructured materials show great potential as an effective electrode material for high-performance supercapacitor applications.

In this doctoral work, we demonstrate an easy and efficient hydrothermal/solvothermal approach for growing nanostructured materials of some transition metal oxides and sulfides for supercapacitor applications. In this regard, the concise aspects of supercapacitors in terms

of charge storage mechanisms and the recent progress in the design and fabrication of electrode materials as well as energy-related performance were described.

In chapter 2, describes all the analysis techniques used in this work.

In chapter 3, we adopt a facile effective single-step hydrothermal process for constructing of $\text{Zn}_{0.76}\text{Co}_{0.24}\text{S}$ microspheres containing nanoflakes-like structure, directly on nickel foam. The obtained electrode exhibited an excellent electrochemical charge storage performance and satisfactory charge/discharge cycling stability compared to the individual mono metal sulfides such as ZnS and CoS . Boosting the synergistic effect resulting from the co-existence of Zn and Co in the binary $\text{Zn}_{0.76}\text{Co}_{0.24}\text{S}$. Moreover, the assembled hybrid supercapacitor of $\text{Zn}_{0.76}\text{Co}_{0.24}\text{S}$ delivered outstanding specific energy comparable or much better than the most recently reported devices. These results indicate the potential of $\text{Zn}_{0.76}\text{Co}_{0.24}\text{S}$ as an electrode material for high-performance supercapacitors.

In chapter 4, we demonstrate the synthesis of ZnCo_2O_4 nanospheres via a one-step, calcination-free H_2O_2 -assisted hydrothermal method. Assembled as a supercapacitor, ZnCo_2O_4 -electrodes showed an excellent capacitive performance with superior cycling stability, showing its promising potential as an efficient electrode material for supercapacitors.

In comparison, The benefit of binary transition metal sulfide ($\text{Zn}_{0.76}\text{Co}_{0.24}\text{S}$) over binary transition metal oxide (ZnCo_2O_4) is the lower electronegativity sulfur atom than oxygen, thus replacing oxygen with sulfur will produce a more electrochemically conductive compound leading to higher storage capacity, but lower cycling performance than binary transition metal oxide.

In chapter 5, we report a facile synthetic solvothermal method for the preparation of FeCo_2O_4 nanosheets, constructing a highly porous structure. This high porosity allowed excellent unique electrochemical performance.

Proposed that the potential of FeCo_2O_4 for supercapacitor applications. For these purposes, the presence of the porous structure will generally provide a highly effective surface area exposed to electrolytes, more active sites for redox reactions, enable effective ion pathways from the electrolyte to electrode active material and facilitate the movement of the electrons through redox reactions.

In chapter 6, we adopt a feasible method to enhance the electrochemical performance of (α -MnS) by incorporating nanostructured α -MnS with an underlying conductivity-supporter reduced graphene oxide (rGO). In this chapter, nanoflakes-like structured α -MnS/rGO was prepared via a facile one-step hydrothermal method. The presence rGO can offer a matrix for α -MnS-nanoflakes suggesting an efficient way to enhance the conductivity. It does not only adapt to the nanoflakes α -MnS by preventing its aggregation, but also offers a large electrode / electrolyte interface for the redox reactions. Therefore, the structure of α -MnS/rGO markedly enhanced electrochemical performance as an electrode material for supercapacitor applications. Suggesting that, introducing carbon materials such as (rGO) is an efficient way to improve the electrochemical performance of mono metal sulfide for energy storage applications.

Content

Abstract.....	I
Content.....	i
Figures caption.....	vii
Tables caption.....	xiv.
Chapter 1. Introduction.....	1
1.1 Historical overview and fundamentals of supercapacitors.....	3
1.2 Charge storage mechanisms in supercapacitors.....	6
1.2.1 Electric double-layer capacitance (EDLCs).....	7
1.2.2 Pseudocapacitors and battery materials.....	9
1.2.2.1 Capacitance vs capacity.....	12
1.3 Supercapacitor vs battery (charge/discharge performance).....	15
1.4 Basic principles of physical capacitors.....	17
1.5 Derivation of some key parameters.....	19
1.5.1 Derivation the capacitance of capacitive electrodes.....	19
1.5.2 Derivation the capacitance of noncapacitive electrodes.....	20
1.5.3 Derivation energy density and power density for capacitive electrode materials.....	20
1.5.4 Derivation energy density and power density for noncapacitive electrode materials.....	22
1.6 Two electrodes vs three electrodes cell set up	23
1.6.1 Classification of Supercapacitors devices.....	23

1.6.2 Mass balance equation between positive and negative electrodes.....	23
1.7 Electrochemical performance of Supercapacitors.....	25
1.7.1 The operating potential window, cell voltage, and the electrolyte.....	25
1.7.1.1 The operating potential window vs cell voltage.....	25
1.7.1.2 Electrolyte	27
1.7.1.3 Full cell voltage of the device.....	29
1.7.2 ESR.....	31
1.7.3 Rate capability.....	31
1.7.4 Stability test (cycling life).....	32
1.7.5 Coulombic efficiency.....	32
1.8 Electrode materials for supercapacitors.....	32
1.8.1 Carbon-based materials.....	33
1.8.2 Metal oxides, sulfides, hydroxides, and nitrides.....	38
1.9 The objective of this work.....	42
Reference: (Chapter 1).....	46
Chapter 2. Experimental Techniques	63
2.1 List of Materials.....	64
2.2 Hydrothermal / solvothermal syntheses techniques.....	65
2.2.1. Hydrothermal synthesis of $\text{Zn}_{0.76}\text{Co}_{0.24}\text{S}$ and its corresponding single metal sulfides (CoS) and (ZnS).....	65

2.2.2. Hydrothermal synthesis of ZnCo_2O_4 Nanospheres	66
2.2.3. Hydrothermal synthesis of FeCo_2O_4 mesoporous nanosheets FCONS.....	67
2.2.4. Hydrothermal synthesis of $\alpha\text{-MnS}$ and $\alpha\text{-MnS-rGO}$	67
2.2.4.1 Synthesis of $\alpha\text{-MnS}$	67
2.2.4.2 Synthesis of $\alpha\text{-MnS/rGO}$	68
2.3 The Instruments and Characterization.....	69
2.3.1 X-ray diffraction (XRD).....	69
2.3.2 Transmission electron microscopy (TEM).....	72
2.3.3 Scanning electron microscopy (SEM).....	74
2.3.4 X-ray photoelectron spectroscopy (XPS).....	75
2.3.5 Surface area measurement.....	77
2.3.6 Cyclic voltammetry.....	77
2.3.7 Galvanostatic charge- discharge studies.....	78
2.6.8 Electrochemical impedance spectroscopy.....	80
References (Chapter 2).....	82
Chapter 3. A Single-Step Synthesis and Direct Growth of microspheres containing the nanoflakes-like structure of $\text{Zn}_{0.76}\text{Co}_{0.24}\text{S}$ as a high-performance electrode for Supercapacitors.....	84
3.1 Introduction.....	84
3.2 Experimental Section.....	86
3.2.1 Materials.....	86
3.2.2 Synthesis of $\text{Zn}_{0.76}\text{Co}_{0.24}\text{S}$	87

3.2.3 Material characterization.....	88
3.2.4 Electrochemical measurements.....	88
3.3 Results and discussions.....	90
3.3.1 Formation mechanism, morphological and structural characterization.....	90
3.3.2 Electrochemical performance.....	100
3.4 Conclusions.....	113
References (Chapter 3).....	114
Chapter 4. One-step, calcination-free synthesis of zinc cobaltite nanospheres for high-performance supercapacitors.....	121
4.1 Introduction.....	121
4.2 Experimental section.....	122
4.2.1 Hydrothermal Synthesis of ZnCo_2O_4	122
4.2.2 Materials characterization.....	123
4.2.3 Electrochemical measurements.....	123
4.3 Results and discussion.....	125
4.3.1 Formation mechanism, morphological and structural characterization.....	125
4.3.2 Electrochemical performance.....	129
3.4 Conclusions.....	137
References (Chapter 4).....	144

Chapter 5. Spinel-Structured FeCo_2O_4 mesoporous nanosheets as efficient electrode for supercapacitor applications	145
5.1 Introduction.....	145
5.2 Materials and methods.....	147
5.2.1 Synthesis of FeCo_2O_4	147
5.2.2 Materials characterization.....	147
5.2.3 Electrochemical performance measurements.....	148
5.3 Results and discussion	
5.3.1 Synthesis and structural analysis.....	149
5.3.2 Electrochemical performance.....	156
5.4 Conclusions.....	160
References (Chapter 5).....	161
Chapter 6. Hydrothermal Synthesis of α -MnS Nanoflakes @ Nitrogen and Sulfur Co-doped rGO for High-Performance Hybrid Supercapacitor.....	169
6.1 Introduction.....	169
6.2 Experimental Section.....	171
6.2.1 Synthesis of α -MnS.....	171
6.2.2 Synthesis of α -MnS/rGO.....	171
6.2.3 Materials characterization.....	172
6.2.4 Electrochemical measurements.....	172
6.3 Results and discussion.....	174
6.3.1 Synthesis and structural analysis.....	174

6.3.2 Electrochemical performance.....	187
6.3.3 Hybrid supercapacitor device fabrication.....	194
6.4 Conclusions.....	198
References (Chapter 6).....	200
Chapter 7. General conclusion.....	206
Scientific Journal Publication list.....	209

Figures Caption

Figure1.1. Ragone plot illustrated the specific power density vs. specific energy density for different electrochemical energy storage systems.....	3
Figure 1.2. Schematic representation of a conventional capacitor (a) and a supercapacitor(b).....	6
Figure 1.3 Different electrochemical energy storage materials (a) EDLC , (b) PCs and (c) Battery type materials, respectively.....	6
Figure 1.4 Schematically representation of the three types of electrode materials used in supercapacitor.....	7
Figure 1.5. Electrochemical behavior of typical electrochemical supercapacitor and typical battery, (a and b) cyclic voltammogram curves and (c and d) galvanostatic charge-discharge curves. ESR: represents equivalent series resistance.....	14
Figure 1.6. Different charge storage mechanisms.....	14
Figure 1.7 Charge–discharge profiles of a battery, an EDLC, and a hybrid device.....	16
Figure. 1.8 Charge–discharge profiles of two supercapacitors that deviate considerably from an ideal capacitive behavior (a) overestimated and (b) underestimated.....	16
Figure 1.9. (V-Q) a plot of a typical capacitor obtained at a constant current for a certain time.....	19
Figure 1.10 Schematic classification of the 2-electrode assembled device.....	24