Centre for Green Energy and Vehicle Innovation

Faculty of Engineering and Information Technology

Centre for Clean Energy Technology

Faculty of Science

Graphene and Metal Oxide Nanomaterials

for High-performance Supercapacitors

A Thesis Presented in Fulfillment of the Requirement for the

Degree of

Doctor of Philosophy

By
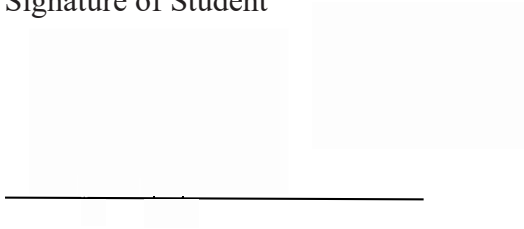
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August 2015

CERTIFICATE OF ORIGINAL AUTHORSHIP

I certify that the work in this thesis has not previously been submitted for a degree nor has been submitted as part of requirements for a degree except as fully acknowledged within the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

Signature of Student

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August 2015

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LIST OF PUBLICATION

1. **Yiying Wei**, Bing Sun, Dawei Su, Jianguo Zhu and Guoxiu Wang. "3D Free-Standing $NiCo_2O_4$@graphene Foam for High-performance Supercapacitors." Advanced Functional Materials, submitted, 2015. (Impact factor: 11.8)

2. **Yiying, Wei**, Shuangqiang Chen, Dawei Su, Bing Sun, Jianguo Zhu, and Guoxiu Wang. "3D mesoporous hybrid $NiCo_2O_4$@graphene nanoarchitectures as electrode materials for supercapacitors with enhanced performances." Journal of Materials Chemistry A 2, no. 21 (2014): 8103-8109. (Impact factor: 7.4)

3. **Yiying, Wei**, Jianguo Zhu, and Guoxiu Wang. "High-Specific-Capacitance Supercapacitor Based on Vanadium Oxide Nanoribbon." (2014). Applied Superconductivity, IEEE Transactions on, 2014, 24, (5), 1-4. (Impact factor: 1.2)

4. **Yiying Wei,** Guoxiu Wang, Jianguo Zhu, "Synthesis and Characterization of Vanadium Oxide Nanotubes as Electrode Materials for Electrochemical Capacitors", ECS Transactions 58 (2014) 61-67.

5. **Yiying Wei**, Shuangqiang Chen, Jianguo Zhu and Guoxiu Wang, "Synthesis and Characterization of Nanoporous $NaMn_2O_4$ electrode Material for Sodium-Ion Battery", 17th International Meeting on Lithium Batteries in Como, Italy, June 10 to 14, 2014.

6. Chen, Shuangqiang, Yufei Zhao, Bing Sun, Zhimin Ao, Xiuqiang Xie, **Yiying Wei**, and Guoxiu Wang. "Microwave-assisted synthesis of mesoporous Co_3O_4 nanoflakes for applications in lithium ion batteries and oxygen evolution reactions." ACS applied materials & interfaces 7, no. 5 (2015): 3306-3313. (Impact factor: 6.7)

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LIST OF SYMBOLS AND ABBREVIATIONS

Abbreviation	Full name
1D	One-dimensional
3D	Three Dimension
ALD	Atomic layer deposition
BET	Brunauer–Emmett–Teller
CAES	Compressed air energy storage
CFC	Controllable freeze casting
CMG	Chemically modified graphene
CNHs	Carbon nanohorns
CNTs	Carbon nanotubes
CPE	Constant phase element
DLCs	Double layer capacitors
EDLCs	Electrochemical double layer capacitors
ESR	Equivalent series resistance
ESSs	Energy storage systems
EVs	Electric vehicles
FES	Flywheel energy storage
FESEM	Field-emission scanning electron microscopy
GONPs	Graphene oxide nanoplatelets
HEVs	Hybrid electric vehicles
ICE	Internal combustion engine
LPCVD	Low-pressure chemical vapor deposition
MWNTs	Multi-walled carbon nanotubes
OHP	Outer Helmholtz Plane
PEI	ployethyleneimine
PHEVs	Plug-in hybrid electric vehicles
PVDC	Ploy vinylidene chloride
SEM	Scanning electron microscopy
SMES	Superconductive magnetic energy storage
SWNTs	Single-walled nanotubes

TEM	Transmission electron microscopy
TMAOH	Tetramethyl ammonium
VN	Vanadium nitride

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ABSTRACT

Energy storage systems (ESSs) play a critical role in plenty of applications including renewable energy systems, power systems for electric vehicles (EVs) and hybrid electric vehicles (HEVs), and electrical power grids for improving reliability and overall use of the entire system. Currently, there are several types ESSs dominated the energy storage. Each kind of ESSs has their own operation mechanism, energy efficiency, energy density, power density, cycle life, charge and discharge capability, cost efficiency, operating temperature. The common ESS is based on lead acid battery which stores electrical energy in the form of chemical energy. However, if the batteries are overdischarged or kept at a discharged state, its capability will be irreversibly undermined because the sulfate crystals become larger and more difficult to break up during recharge. Since the first NiCd battery was created by Waldemar Jungner in 1899, even though NiCd battery technologies have experienced a series of evolutionary developments, its demerits are obvious including 1) shorter life cycle; 2) memory effect; 3) toxicity of Cd; 4) lower energy density; and 5) limited negative temperature coefficient. Based on the development of NiCd battery technology, nickel metal hydride (NiMH) batteries was proposed by researchers which possess better performance than NiCd batteries in cycle life, energy density and charge&discharge rates. Lithium ion is the preferred chemistry, having a superior specific energy and power density to nickel metal hydride. More lithium per gram stored in the electrodes contributes to higher energy density and power density. In addition to chemical battery system, researchers recently proposed some new sorts of ESSs including flywheel, compressed air energy storage (CAES), superconductive magnetic energy storage (SMES), etc. All of them can provide super energy density and power density. But they are more or less blocked ether in complex mechanical

construction or cooling device.

Supercapacitor has emerged to be an exciting energy storage device, which is able to provide high specific power, charge and discharge up to million times, have long lifetime and broad range of working temperature. Even though supercapacitor has been widely seen as a promising energy storage candidate to replace the traditional chemical batteries, it also suffer its drawback that the low energy density (the energy stored in per unit of volume and weight), high equivalent series resistance (ESR) and its high cost associated with its performance.

Therefore, this PHD thesis project aims to address these drawbacks of supercapacitor by designing different nanotechnologies and fabrication methods to synthesize advance materials with better performance than that of conventional supercapacitor. A Series of designed structures and materials were fabricated by designed methods. All the materials were also investigated by using X-ray diffraction, scanning electron microscopy (SEM), transmission electron microscopy (TEM) observation techniques, Brunauer–Emmett–Teller (BET) surface area measurement and electrochemical testing.

A facile and effective hydrothermal treatment that is able to control the condensation speeds of precursors in the solution along the <010>, <100> and <001> directions was designed to fabricate vanadium oxide nanoribbon used for the electrode of supercapacitor. It was achieved by controlling the hydrothermal reaction time and the weight ratio to synthesize the ultralong vanadium oxide nanoribbon with controlled width. It has high specific capacitance of 453 F g^{-1} at the scam rate of 2 mV s^{-1} in 2 M NaCl electrolyte, and it still maintained a high capacitance of 201 F g^{-1} at a higher scan rate of 50 mV s^{-1}, attributing to the easy ion insertion and electronic transport along the a-b plane rather through the layers of the c-axis.

Vanadium oxide nanotubes were synthesized by a revised hydrothermal treatment with high-speed stirring. The preparation involved dissolution of V_2O_5 into H_2O_2 and high-speed stirring (10000 r/min) with hexadecylamine. The product was characterized by scanning electron microscopy, transmission electron microscope, X-ray diffraction and thermogravimetric analysis. The electrochemical properties of the materials as electrodes for electrochemical capacitors were evaluated by cyclic voltammetry in a three electrode system consisting of a saturated calomel electrode as reference electrode, platinum as a counter electrode and the active materials as the working electrode. A high capacitance of 148.5 F g^{-1} was obtained at a scan rate of 2 mV s^{-1} in 2M KCl. The electrode maintained a high capacitance of 105 F g^{-1} at a higher scan rate of 50 mV s^{-1} in 2M KCl electrolyte.

3D mesoporous hybrid $NiCo_2O_4$@graphene nanoarchitectures were successfully synthesized by a combination of freeze drying and hydrothermal reaction. Field-emission scanning electron microscopy (FESEM) and TEM analyses revealed that $NiCo_2O_4$@graphene nanostructures consist of a hierarchical mesoporous sheet-on-sheet nanoarchitecture with a high specific surface area of 194 m^2 g^{-1}. Ultrathin $NiCo_2O_4$ nanosheets, with a thickness of a few nanometers and mesopores ranging from 2 to 5 nm, were wrapped in graphene nanosheets and formed hybrid nanoarchitectures. When applied as electrode materials in supercapacitors, hybrid $NiCo_2O_4$@graphene nanosheets exhibited a high capacitance of 778 F g^{-1} at the current density of 1 A g^{-1}, and an excellent cycling performance extending to 10000 cycles at the high current density of 10 A g^{-1}.

We also presented a rational, large-scale and general method, called controllable freeze casting (CFC), to fabricate a high-densely assembled and aligned free-standing $NiCo_2O_4$@graphene 3D foam by vacuum filtration and air compress pressure assembly method. In the designed method, the amount of water is controllable, therefore controlling

the size and the shape of the ice when the material was introduced into freeze drying system, finally achieving controllable pore size and aligned structure. This free-standing foam retains the intrinsic properties of graphene sheet, such as high surface area and high electrical conductivity. In the foam, the graphene sheets build the high conductive skeletons. And the skeletons with high surface areas support the uniform distribution of $NiCo_2O_4$ nanoparticles on the graphene sheets. By controlling the amount of water in the precursor, it is possible to fabricate 3D $NiCo_2O_4$@graphene foams with a wide range of thickness and pore size. This dense $NiCo_2O_4$@graphene material exhibited a high capacitance of 790 F g^{-1} at a current density of 2 A g^{-1}, and an excellent cycling performance at a high current density of 10 A g^{-1}. The compression test revealed that the 3D $NiCo_2O_4$@graphene foam exhibited strong mechanical property which is able to support 20,000 times its own weight without structure collapsing. The novel synthesis method of such 3D foam with excellent properties paves the way to explore the application of lamellar materials like graphene in a self-supporting, metal oxide deposition and 3D foam.