REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*
26-02-2015

2. REPORT TYPE
Final

3. DATES COVERED *(From - To)*
07-01-2011 - 11-30-2014

4. TITLE AND SUBTITLE
High Efficiency Flexible Battery based on Graphene-Carbon Nanotube Hybrid Structure

5a. CONTRACT NUMBER

5b. GRANT NUMBER
FA9550-11-1-0135

5c. PROGRAM ELEMENT NUMBER

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

6. AUTHOR(S)
Jiuhua Chen, Wonbong Choi

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Florida International University, 11200 S W 8TH ST MARC 430, Miami, FL 33199
University of North Texas, Denton, Texas 76203-5017

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
AF OFFICE OF SCIENTIFIC RESEARCH
875 NORTH RANDOLPH STREET, RM 3112
ARLINGTON VA 22203

10. SPONSOR/MONITOR'S ACRONYM(S)
AFOSR

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
A: approved for public release

13. SUPPLEMENTARY NOTES

14. ABSTRACT
The following achievements have been make during this project: •A binder-free interface controlled CNTs based anode on Cu were synthesized-very high 1st cycle capacity (~ 2500 mAh/g), at 1C (~ 900 mAh/g) and at 3C rates (767 mAh/g), and high capacity retention at 1C rate for 50 cycles. • Demonstrated a large scale flexible graphene electrode • Fabricated an array structure of 3D CNTs-graphene on transparent and flexible polyethylene terephthalate (PET) film through a simple lamination process- structural integrity, low contact resistance, excellent C-rate capability and high Coulombic efficiency of over 99%. • Multi-layered structure of Gr/Si-QDs anodes have been successfully fabricated- initial discharge capacity of 2869 mAh/g at 0.5 C and 895 mAh/g, 1C over 200 cycles.• Graduated 2 Ph.D. students, 2 undergraduate student
• Students received awards from international conferences: Awarded Graduate Excellence in Materials Science (GEMS) Award American Ceramic

15. SUBJECT TERMS
Carbon nanotube; graphene; electrode; battery.

16. SECURITY CLASSIFICATION OF: a. REPORT	b. ABSTRACT	c. THIS PAGE	17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
U	U	U	UU	9	Jiuhua Chen
					19b. TELEPHONE NUMBER *(Include area code)* 305-348-3140

Final Report

Title: High Efficiency Flexible Battery based on Graphene-Carbon Nanotube Hybrid Structure

Award number: FA9550-11-1-0135
PI: Prof. Jiuhua Chen (Florida International University)
Sub-contract: Prof. Wonbong Choi (Univ. of North Texas)
Duration of project: 07/01/11 - 11/30/14,
Budget:$405,426
Achievements:

- A binder-free interface controlled CNTs based anode on Cu were synthesized-very high 1st cycle capacity (~ 2500 mAh/g), at 1C (~ 900 mAh/g) and at 3C rates (767 mAh/g), and high capacity retention at 1C rate for 50 cycles.
- Demonstrated a large scale flexible graphene electrode
- Fabricated an array structure of 3D CNTs-graphene on transparent and flexible polyethylene terephthalate (PET) film through a simple lamination process- structural integrity, low contact resistance, excellent C-rate capability and high Coulombic efficiency of over 99%.
- Multi-layered structure of Gr/Si-QDs anodes have been successfully fabricated- initial discharge capacity of 2869 mAh/g at 0.5 C and 895 mAh/g, 1C over 200 cycles.
- Graduated 2 Ph.D. students, 2 undergraduate student
- Students received awards from international conferences: Awarded Graduate Excellence in Materials Science (GEMS) Award American Ceramic Society (MS&T 2011) MRS best poster award (2013 Fall MRS meeting)
- 12 journal papers, +20 conference presentations, proceedings, book chapters
- Graphene Book

Publications:

1. Multi Layered Si-CuO Quantum Dots Wrapped by Graphene for High-Performance Anode Material in Lithium- Ion Battery, B. Rangasamy, J. Hwang, W Choi, Carbon 77 1065(2014)
2. Hierarchical NiCo2O4@nickel-sulfide nanoplate arrays for high-performance supercapacitors, Chu Q, Wang W, Wang X, Yang B, Liu X, Chen J, Journal of Power Sources 267: 19–25 (2014)
3. Large Scale Patternable 3-Dimensional Carbon Nanotube-Graphene Structure for Flexible Li-ion Battery, C W Kang, R Baskaran, J Y Hwang, B C Ku, W B Choi, Carbon 68. 493 (2013)
4. Multiwall Carbon Nanotube Based Anodes on 3D Current Collector for Li-Ion Batteries. C. Kang, W. Choi, Journal of Power Sources 219, 364 (2012)
5. Three-dimensional carbon nanotube-graphene hybrids on porous nickel films for device fabrication. Z. Yan, W. Choi, P. Ajayan, J. Tour, ACS Nano (2012)
6. Ultra-high current density multiwall carbon nanotube field emitter structure on three-dimensional micro-channeled copper, Appl. Phys. Lett. (2012)

7. Carbon Nanostructures in Lithium Ion Batteries: Past, Present and Future. Critical Reviews in Solid State and Materials Sciences, I. Lahiri, W. Choi, Critical Review Sold. Stat. Dev. **128-166,** Volume 38, 2013
8. Ultrathin alumina coated carbon nanotubes as negative electrodes for high capacity and safe Li-ion battery, Indranil Lahiri, Seung-Min Oh, Jun Y. Hwang, Chiwon Kang, Hyeongtag Jeon, Rajarshi Banerjee, Yang-Kook Sun, Wonbong Choi, J. Mater. Chem., 2011
9. Multiwall Carbon Nanotube Based Anodes on 3D Current Collector for Li-Ion Batteries. Chiwon Kang, Indranil Lahiri, Rangasamy Baskaran, Jun Y. Hwang, Won-Gi Kim, Yang-Kook Sun, Rajarshi Banerjee, Wonbong Choi, Journal of Power Sources, 219, 364 (2012)
10. Synthesis and characterization of self-organized multilayered graphene-carbon nanotube hybrid films, Santanu Das,a Raghunandan Seelaboyina,a Ved Verma,a Indranil Lahiri,a Jun Yeon Hwang,b Rajarshi Banerjeeb and Wonbong Choi* J. Mater. Chem., 2011, 21 (20), 7289
11. Carbon Nanotubes: How strong is their bond with the substrate?, Indranil Lahiri, Debrupa Lahiri, Sungho Jin, Arvind Agarwal, Wonbong Choi, ACS Nano 4, 3440 (2010)
12. An all-graphene based transparent and flexible field emission device, Lahiri, W. Choi, Carbon 49. 1614 (2010)
13. Large-area graphene on polymer film for flexible and transparent anode in field emission device, Ved Prakash Verma, Santanu Das, Indranil Lahiri and Wonbong Choi, Appl. Phys. Lett. 96 203108 (2010)
14. Wonbong Choi and Jo-won Lee, Graphene:Synthesis and Applications, CRC Press ISBN-10: 1439861870 | ISBN-13: 978-1439861875 | Publication Date: October 11, 2011 Handbook of Nanomaterials Properties, Carbon Nanomaterials: a review, Nitin Choudhary, Sookhyun Hwang, Wonbong Choi, Springer (2013)
15. Santanu Das and Wonbong Choi, Graphene Synthesis, Graphene: Synthesis and Applications; Series: Nanomaterials and their Applications CRC Press, Published October 2011.

Task I. Large Scale Patternable 3-Dimensional Carbon Nanotube-Graphene Structure for Flexible Li-ion Battery

There has been strong interest in flexible, lightweight and reliable rechargeable batteries to meet the requirements of today's portable devices. To build such flexible rechargeable batteries with high efficiency, new architectures for current collectors need to be developed. The porous 3-dimensional (3D) electrode architecture has been proposed to increase the efficiency of a Li-ion battery by using its higher surface area, shorter diffusion path and higher volumetric capacity than those of 2D electrodes. Herein we fabricated an array structure of 3D multiwall carbon nanotubes (MWCNTs)-graphene on transparent and flexible polyethylene terephthalate (PET) film through a simple lamination process. The transferred 3D column structure of MWCNTs onto graphene-PET film showed structural integrity and low contact resistance at high angle bending. The new flexible 3D MWCNTs-graphene-PET electrode yielded excellent C-rate capability and specific capacity with high Coulombic efficiency of over 99%. The novel 3D MWCNTs-graphene nanostructure fabricated on flexible film could provide a wide range of applications in next-generation flexible and light weight batteries and energy storages.

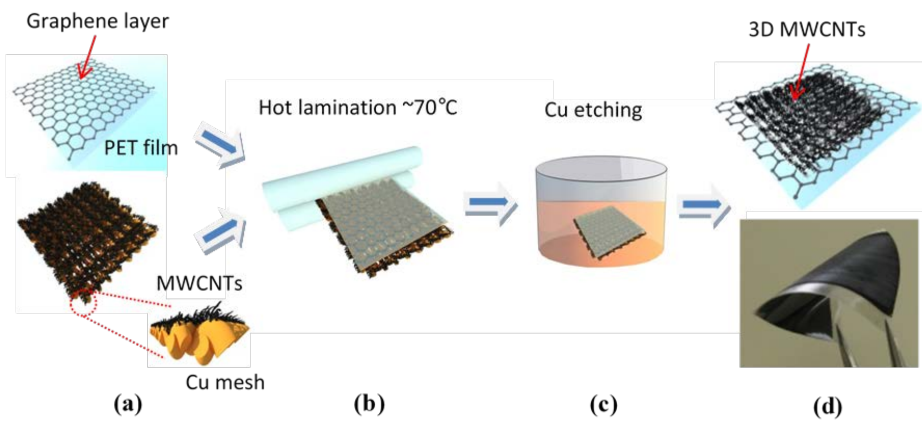


Fig. Process flow of transferring technique of 3D MWCNTs-Cu mesh onto the transparent flexible graphene-PET substrate. (a) Hot laminated graphene-PET film and 3D MWCNTs on Cu mesh directly grown by CVD, (b) Hot lamination of 3D MWCNTs onto graphene-PET, (c) Etching process of Cu mesh by using FeCl3 oxidation acid, (d) 3D pattern of MWCNTs transferred on the graphene-PET film. The digital image shows high flexibility of the 3D MWCNTs-graphene-PET films.

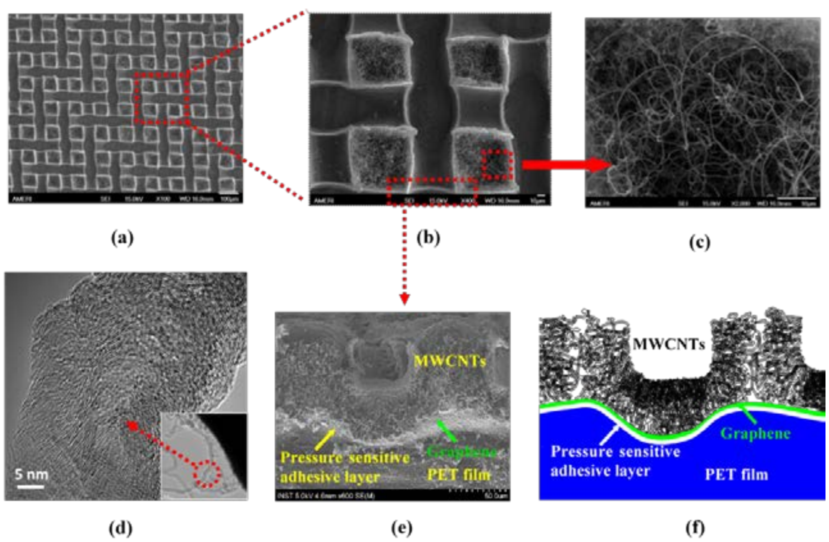


Fig. Structural analysis of as-fabricated 3D MWCNTs-graphene-PET film. (a) The SEM plane view of 3D MWCNTs-graphene-PET film, (b) Zoomed-in SEM image showing detailed morphology of the structure, (c) The magnified SEM image of the randomly oriented MWCNT structures in the patterned structure, (d) HRTEM image of the MWCNTs grown on 3D Cu mesh showing a herringbone-like internal structure, (e) The cross-sectional SEM image of 3D MWCNTs-graphene-PET film, (f) Schematic diagram (not to scale) of the cross-sectional image.

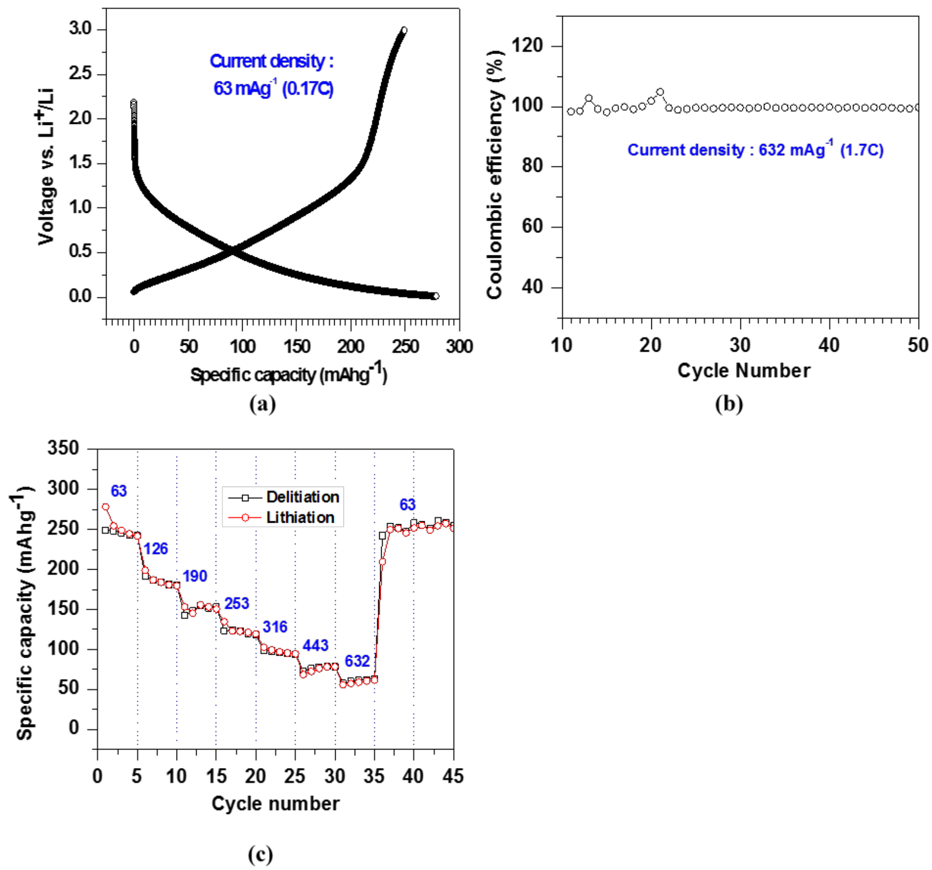


Fig. Electrochemical performance of the 3D MWCNTs-graphene-PET as a flexible LIB anode structure. (a) Initial galvanostatic charge and discharge profiles of 3D MWCNTs-graphene-PET film anode structure, (b) Coulombic efficiency of the anode at 1.7C, (c) C-rate capability of the anode at seven different current densities. Numerical values represent current densities, at which charge and discharge cycles were conducted.

Task II. 3 Dimensional Carbon Nanotube for Li-Ion Battery Anode

Carbon nanotubes, in different forms and architectures, have demonstrated good promise as electrode material for Li-ion batteries, owing to large surface area, shorter Li-conduction distance and high electrical conductivity. However, practical application of such Li-ion batteries demands higher volumetric capacity, which is otherwise low for most nanomaterials, used as electrodes. In order to address this urgent issue, we have developed a novel 3-dimensional (3D) anode, based on multiwall carbon nanotubes (MWCNTs), for Li-ion batteries. The unique 3D design of the electrode allowed much higher solid loading of active anode material, MWCNTs in this case and resulted in more amount of Li+ ion intake in comparison to those of conventional 2D Cu current collector. Though one such 3D anode was demonstrated to offer 50% higher capaci-ty, compared to its 2D counterpart, its ability to deliver much higher capacity, by geometrical modification, is presented. Furthermore, deposition of amorphous Si (a-Si) layer on the 3D electrode (a-Si/MWCNTs hybrid structure) offered en-hancement in electrochemical response. Correlation between electrochemical performances and structural properties of the 3D anodes highlights the possible charge transfer mechanism.

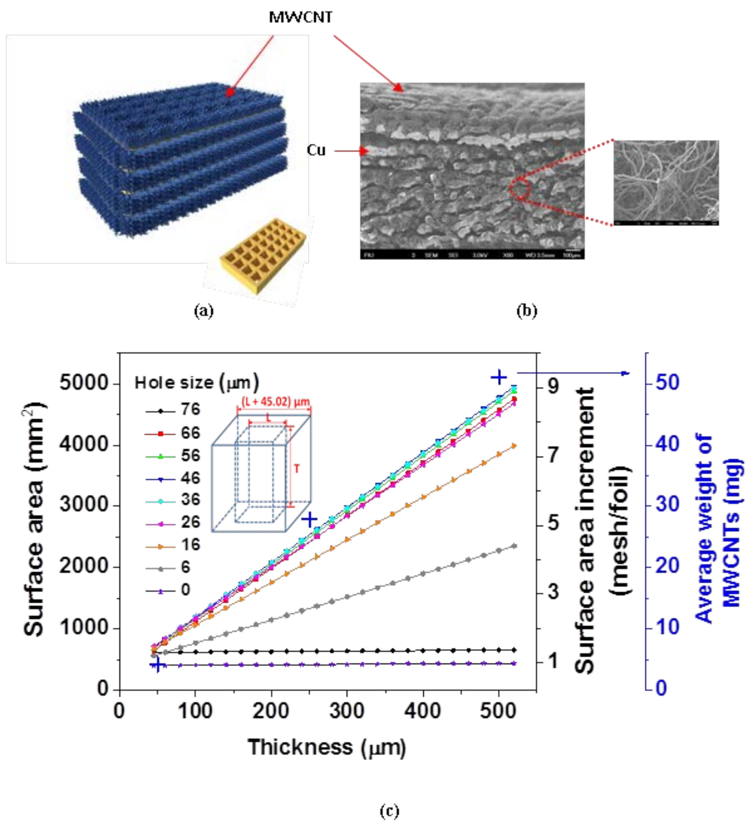


Figure (a) A schematic model of an anode stack assembled using 4 numbers of converteuniform stacking cuboid arrays from the geometry of a real 3D Cu mesh (The bottom right inset shows a unit cell of the cuboid arrays.), (b) SEM images exhibiting a cross-section perpendicular to the anode system stacked by 9 individual MWCNTs on 3D Cu mesh and highly entangled structures of MWCNTs, (c) The surface area and its increment of the 3D Cu mesh and the 2D Cu foil and the average real weight of MWCNTs as a function of different thickness and hole sizes (The inset illustrates a unit cell of the 3D Cu mesh with its dimension.).

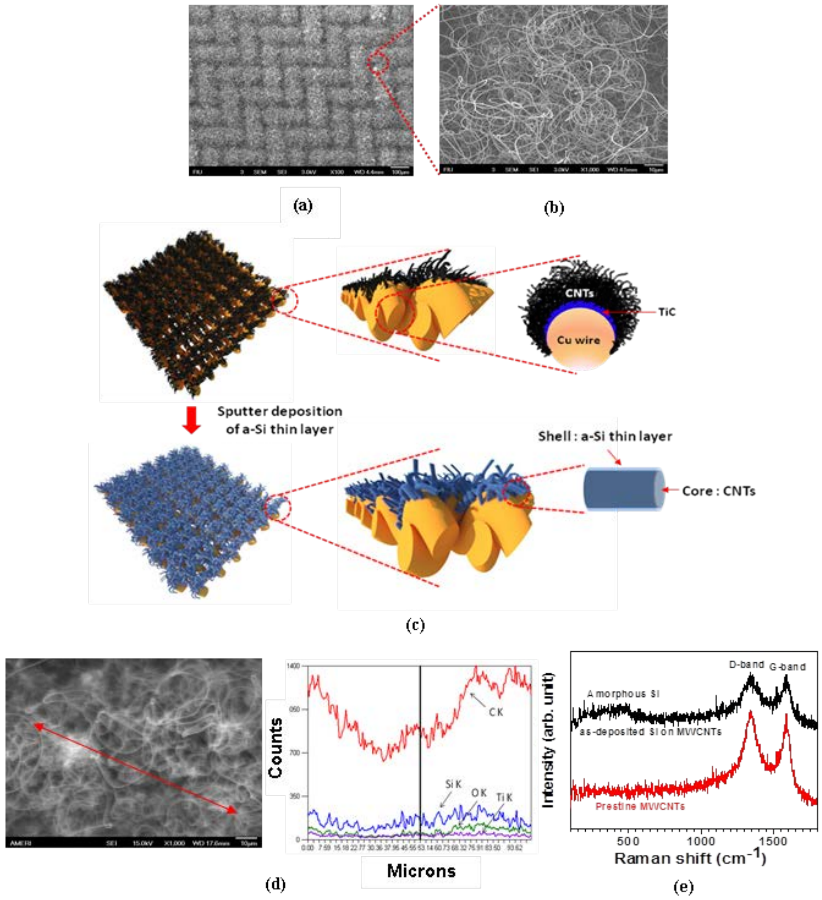


Figure. Morphology and structure of the proposed anode systems. (a) A plane view of SEM image showing the MWCNTs covered on the 3D Cu mesh, (b) The threadlike grass structures of MWCNTs on the 3D Cu mesh with their diameter in the range of 200 - 300 nm, (c) Schematic diagram (not to scale) of the geometry of the MWCNTs grown on the 3D Cu mesh and the a-Si deposited MWCNTs structure on the 3D Cu mesh, (d) EDS elemental analysis of the a-Si/MWCNTs hybrid structure in the linearly selected area across the SEM image, (e) Raman spectroscopic response indicating high defect den-sity of MWCNTs according to ID/IG ratio around 1 and the amorphous Si peak at around 480 cm-1 in the a-Si/MWCNTs.

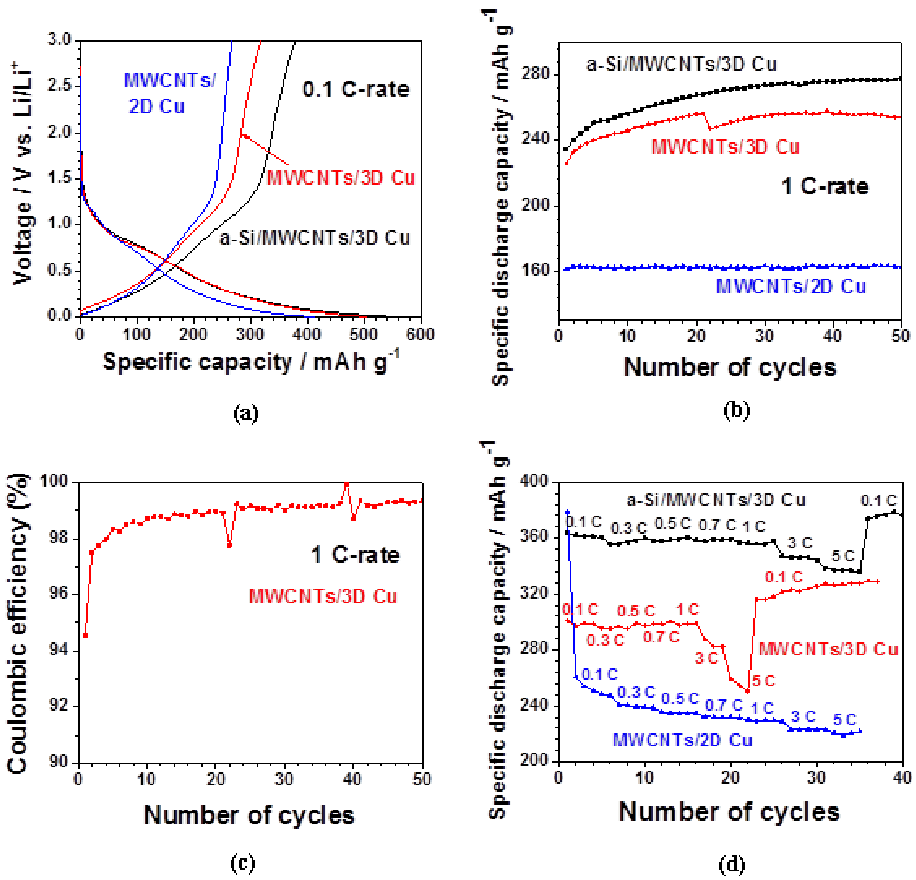


Figure. Electrochemical performance of the anode structures of as-grown MWCNTs on 3D Cu mesh, MWCNTs on 2D Cu foil and a-Si/MWCNTs core-shell composite on 3D Cu mesh. (a) First charge-discharge cycle at 0.1 C-rate, (b) Com-parison of the cycling stability of the different anode structures, (c) Coulombic efficiency at 1 C-rate, (d) The variation of reversible capacities at different C-rates.

Task III. High capacity and excellent stability of lithium ion battery anode using interface-controlled binder-free MWCNT grown on copper

We present a novel binder-free multi-wall carbon nanotube (MWCNT) structure as anode in Li-ion batteries. The interface-controlled MWCNT structure, synthesized through a two-step process of catalyst deposition and chemical vapor deposition (CVD) and directly grown on copper current collector, showed very high specific capacity - almost three times as that of graphite, excellent rate capability – even at a charging/discharging rate of 3C and nil capacity degradation up to 50 cycles. Significantly enhanced properties of this anode could be related to high Li-ion intercalation on CNT walls, strong bonding with substrate and excellent conductivity.

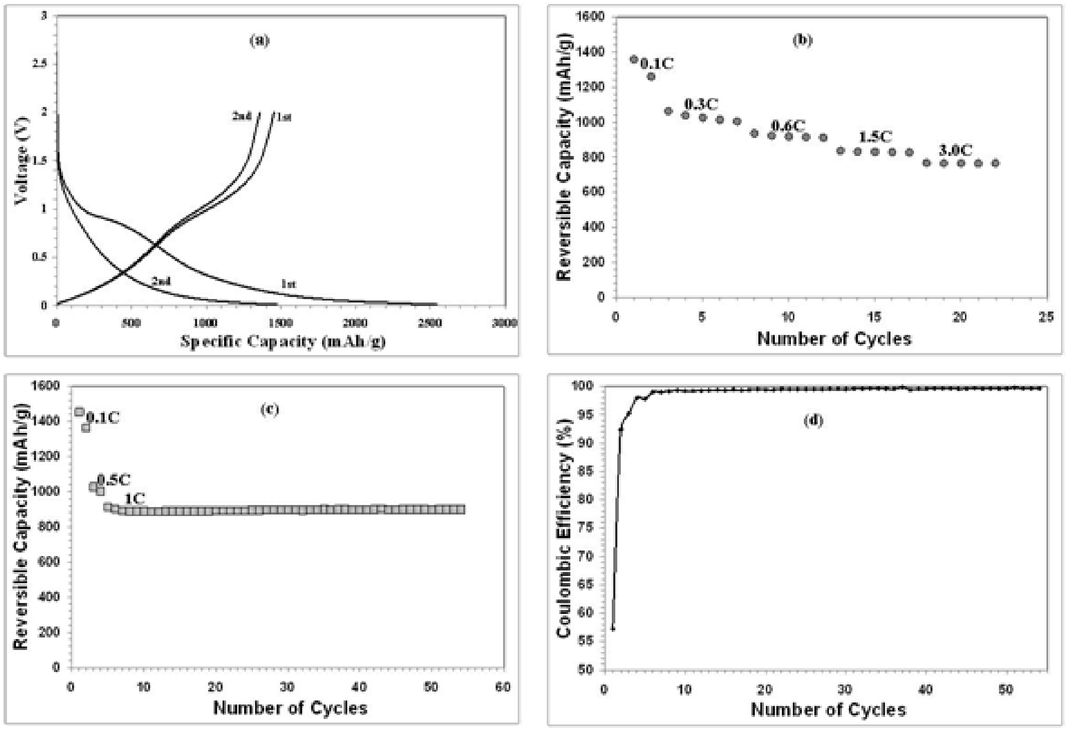
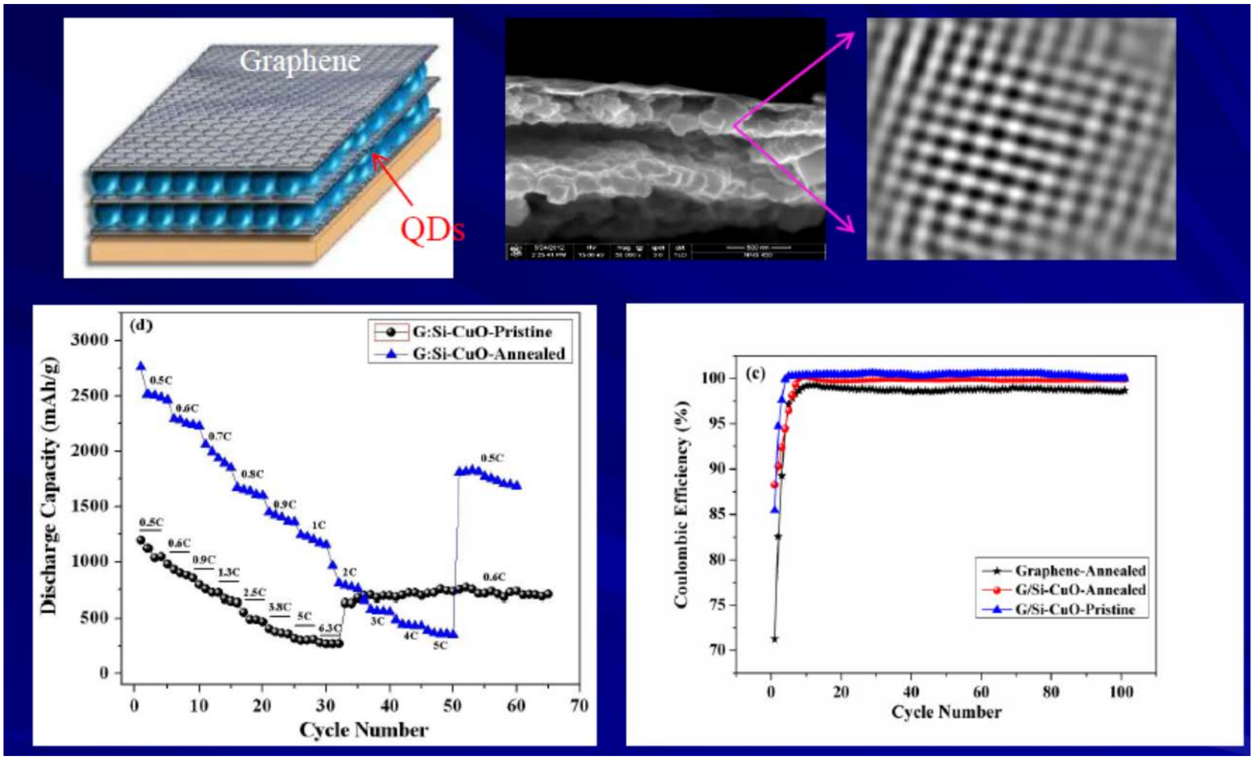


Figure. Electrochemical characteristics of the proposed CNT-based electrode structure. (a) First two charge-discharge cycles of the MWNT-on-Cu anode, at 0.1C rate. The first discharge cycle (lithiation) has shown a very high capacity of 2547 mAhg-1, while the following de-lithiation cycle showed specific capacity of 1455 mAhg-1. (b) Reversible capacity of the MWNT-on-Cu anode, at different C-rates. Very high specific capacity could be observed at all C-rates. Even at 3C rate, a reversible capacity of 767 mAhg-1 was observed, which is almost 2 times the theoretical capacity of graphite. (c) Exceptional stability of the reversible capacity (~ 900 mAhg-1) of the MWNT-on-Cu anode in long-run, at 1C rate. Except first two cycles, virtually no capacity degradation was observed for this anode structure, in 50 cycles. (d) Coulombic efficiency of the MWNT-on-Cu anode, showing very high efficiency, except for the first cycle. After initial 5 cycles, the efficiency remained more than 99%.

Task IV. Multi Layered Si-CuO Quantum Dots Wrapped by Graphene for High-Performance Anode Material in Lithium- Ion Battery

Various approaches to improve the efficiency of Lithium ion batteries (LiB) by using Si have been suggested because Si has the highest known lithium capacity. Although Si is more than ten times higher capacity than existing graphite anodes, Si anodes have limited applications due to its high volume change during cycling. Here we demonstrated graphene/Si-CuO quantum dots (Gr/Si-CuO QD) layered structure as an efficient LiB anode which prevents large volume expansion of Si due to the presence of CuO-Cu_3Si. By ElectroPhoresis Deposition technique, the multi-layer of graphene and Si-CuO QD has been successfully fabricated followed by annealing process to form Cu3Si interlayer as confirmed by High Resolution Transmission Electron Microscope-Energy Dispersive Spectroscopy, X-ray diffraction and Raman analyses. The annealed Gr/Si-CuO QD exhibit the initial gravimetric specific capacity of 2,869 mAhg-1 which is five times higher than that of annealed graphene at 0.5C. After 100 cycles at 1C rate the capacity retains ~71% and the excellent rate capability even at high C rate reveals controlled volume expansion owing to the multi layered architecture and the Cu_3Si inter layer. The layered structure of Gr/Si-CuO QD electrode could be applied in next generation micro power sources.



Scheme of multilayer Graphene/Si-QDs and its SEM and TEM images (top images), C-rate capability of annealed Graphene/Si QDs. Multi-layered structure of Gr/Si-QDs anodes have been successfully fabricated and demonstrated very high initial discharge capacity of 2869 mAh/g at 0.5 C and 895 mAh/g, 1C over 200 cycles.

Future Plans:

We are aiming to overcome some of the key challenges and develop a flexible smart rechargeable battery for next generation energy storages:

- Fabrication of 3D graphene-CNT film based flexible Li-sulfur or Li-air battery,
- Assembly of polymer electrolytes, anode and cathode for (full cell) flexible smart secondary batteries,
- Fabrication of smart battery cells integrated with the lightning protective layer.