RGC Ref.: X-HKUST603/14
(please insert ref. above)

The Research Grants Council of Hong Kong
SFC/RGC Joint Research Scheme
Completion Report

(Please attach a copy of the completion report submitted to the Scottish Funding Council by the Scottish researcher)

Part A: The Project and Investigator(s)

1. Project Title

3D graphene-nanotube hybrid for charge storage

2. Investigator(s) and Academic Department/Units Involved

	Hong Kong Team	Scottish Team
Name of Principal Investigator *(with title)*	Prof. Zhengtang LUO	Dr. Paul Alexander Connor
Post	Assistant Professor	Senior Researcher and Lecturer
Unit / Department / Institution	Dept of Chemical & Biomolecular Engineering, The Hong Kong University of Science and Technology	School of Chemistry, University of St Andrews
Contact Information	keztluo@ust.hk	pac5@st-andrews.ac.uk
Co-investigator(s) *(with title and Institution)*		

3. Project Duration

	Original	Revised	Date of RGC/ Institution Approval *(must be quoted*)
Project Start date	1/1/2015		
Project Completion date	31/12/2015		
Duration *(in month)*	12		
Deadline for Submission of Completion Report	31/12/2016		

Part B: The Completion Report

5. Project Objectives

5.1 Objectives as per original application

1. To design and synthesize 3D graphene-nanotube hybrid structures. New methods will be tested to control the Fe, Ni, or Co seed size with the aim of adjusting the diameter of the carbon nanotube in 3D graphene-nanotube hybrid structures.

2. To evaluate the influence of CVD synthesis parameters on the structure and properties of obtained material.
3. To design, fabricate and test supercapacitors and gain a fundamental understanding of the kinetics and interaction between graphene and charged ions.

5.2 Revised Objectives

Date of approval from the RGC: _____

Reasons for the change: _____

_____

1.
2.
3. ....

6. Research Outcome

Major findings and research outcome
(maximum 1 page; please make reference to Part C where necessary)

For this project we have been focused on the preparation of graphene 3D graphene-nanotube hybrid structures, the understanding of the relevant chemical physics, and the use of them for multiple applications. Our research has been resulted 6 research articles that are published in top-notch journals, including ***Analytica Chimica Acta, J. Power Sources, Chem. Mater., RSC Adv., Carbon, Nanoscale***.

We have carefully studied the growth of single crystalline graphene by tuning the reaction kinetics and relevant parameters. For fuel cell application, we demonstrate that methanol permeability of the nafion/graphene/nafion membrane have a 68.6% decrease in comparison to Nafion membrane. Additionally, we have demonstrated that the fabrication of a graphene-based field effect transistor (GFET) incorporated in a two-dimensional paper network format (2DPNs). The fabricated device is shown to behave similarly to a solution-gated GFET device with enhanced electron and hole mobilities.

After the graphene is synthesized, we demonstrate the transferring method to detach graphene from the catalytic substrate, while retaining structural integrity. We demonstrate that CVD grown graphene on copper can be fully decoupled from the substrate by immersion in water, without significant damage to graphene. We find that the decoupling starts from the graphene edges and defect sites, assisted by interfacial copper oxidation and water intercalation due to galvanic corrosion.

For obtained carbon structures, we have demonstrated that atomic registry has a strong impact on the electronic structure and properties of graphene due to its localized strain and localized charge distribution. The relative reaction rate for grafting diazonium salts on tBLG is much faster than that on AB-stacking graphene. Our results suggest a

venue to separate and sort different stacking modes of bilayer graphene for various promising applications in nanoelectronics.

We developed a method to prepare a controllable and reproducible active substrate for surface enhanced Raman scattering (SERS) using a facile oxidation method that allows us to obtain a titanium oxide (TiO2) capping layer with the desired thickness on nickel–titanium alloy (NiTi). The method can be adapted to exploit the recent advances in molecular vibration study and biomolecular detection due to the versatility of the proposed substrate.

In addition, we have demonstrated a self-assembled pentacene monolayer between the solid-solid interface of few-layered graphene (FLG) and the mica substrate, through a diffusion-spreading method. We found that the formation of a monolayer is kinetically favored by using a 2D Ising lattice gas model for pentacene trapped between the graphene-substrate interfaces.

Potential for further development of the research and the proposed course of action *(maximum half a page)*

Due to the success of this collaborative work, we deem that it is imperative to continue to along this direction to achieve high performance energy storage devices, especially aiming at improving the energy efficiency of fuel cells, utilizing strength of both research groups. In addition, we propose to incorporate 3D graphene-carbon nanotube hybrid material to design/fabricate electrochemical device for other applications such as hydrogen generation, catalysis, etc.

This successful continue of this project will establish new methodologies in creating multifunctional materials and in harvesting their exceptional surface and electric properties for multiple applications. This cross-disciplinary research program combing the capabilities in chemistry and fuel cell to attack a new problem area and promotes collaboration of scientists in Scotland and Hong Kong.

7. The Layman's Summary

(describe <u>in layman's language</u> the nature, significance and value of the research project, in no more than 200 words)

In this project, we have successfully demonstrated a novel experimental methodology to create a new family of graphene nanostructures, *i.e.* 3D graphene-nanotube hybrid, for energy/charge storage, particularly for supercapacitor applications. The produced new structure is unique in that they are able to provide exceptional out-of-plane, electrical and thermal transport in the direction perpendicular to the graphene plane, while still being able to maintain exceptional in-plane electrical, mechanical and surface properties. This Scotland-Hong Kong joint support grants enables us to develop a scientific framework to create a new family of graphene materials, as well as a to gain a fundamental scientific understanding of the controlled synthesis of 3D graphene-nanotube hybrid structures with a desired set of physical and chemical properties.

Part C: Research Output

8. Peer-reviewed journal publication(s) arising directly from this research project

(Please attach a copy of each publication and/or the letter of acceptance if not yet submitted in the previous progress report(s). All listed publications must acknowledge RGC's funding support by quoting the specific grant reference.))

The Latest Status of Publications				Author(s) *(**bold** the authors belonging to the project teams and denote the corresponding author with an asterisk*)*	Title and Journal/ Book *(with the volume, pages and other necessary publishing details specified)*	Submitted to RGC *(indicate the year ending of the relevant progress report)*	Attached to this report *(Yes or No)*	Acknowledged the support of this Joint Research Scheme *(Yes or No)*	Accessible from the institutional repository *(Yes or No)*
Year of publication	Year of Acceptance *(For paper accepted but not yet published)*	Under Review	Under Preparation *(optional)*						
2016				**Cagang, A.A.; Abidi, I.; Tyagi, A**.; Hu, J.; Xu, F.; Lu, T.; **Luo, Z.***	Graphene-based Field Effect Transistor in Two-dimensional Paper Networks, ***Analytica Chimica Acta***, , 917, 101-126	31-Dec-2015	Y	Y	Y
2016				Yan, X.; **Wu, R.;** Xu, J.; **Luo, Z.**; Zhao, T.S.*	A Monolayer Graphene Sandwiched Membrane for Direct Methanol Fuel Cells, ***J. Power Sources,*** 311, 188–194	31-Dec-2015	Y	Y	Y
2016				**Ding, Y.**; Peng, Q.; Gan, L.; **Wu, R.; Ou, X.; Zhang, Q. and Luo, Z.***;	Stacking Modes Induced Reactivity Enhancement for Twisted Bilayer Graphene, ***Chem. Mater.***, 28 (4), 1034–1039	31-Dec-2015	Y	Y	Y
2016				**Abidi, I.H.; Cagang, A.A.; Tyagi, A.; Riaz, M.A.; Wu, R.;** Sun, Q.; **Luo, Z.***	Oxidized Nitinol Substrate for Interference Enhanced Raman Scattering of Monolayer Graphene, ***RSC Adv.***, 6, 7093 - 7100	31-Dec-2015	Y	Y	Y

2016				**Wu, R.;** Gan, L.; **Ou, X.; Zhang, Q.; Luo, Z.***	Detaching graphene from copper substrate by oxidation-assisted water intercalation, ***Carbon***, 2016, 98,138–143	31-Dec-2015	Y	Y	Y
2015				**Q. Zhang,** B. Peng, P.K.L. Chan and **Z. Luo***,	A pentacene monolayer trapped between graphene and a substrate, ***Nanoscale***, 7, 14663-14668	31-Dec-2015	Y	Y	Y

9. Recognized international conference(s) in which paper(s) related to this research project was/were delivered *(Please attach a copy of each delivered paper. All listed papers must acknowledge RGC's funding support by quoting the specific grant reference.)*

Month/Year/ Place	Title	Conference Name	Submitted to RGC *(indicate the year ending of the relevant progress report)*	Attached to this report *(Yes or No)*	Acknowledged the support of this Joint Research Scheme *(Yes or No)*	Accessible from the institutional repository *(Yes or No)*

10. Student(s) trained *(Please attach a copy of the title page of the thesis.)*

Name	Degree registered for	Date of registration	Date of thesis submission/ graduation
Yao Ding	MPhil	1/9/2013	1/8/2015

11. Other impact *(e.g. award of patents or prizes, collaboration with other research institutions, technology transfer, etc.)*

The work supported by this grant has enabled us to collaborate with University of St Andrews on energy research field. Discussion among the two groups has sparked innovations in energy research including fuel cells and supercapcitors. In addition, we are actively looking for more collaborations