RGC Ref.: N_HKUST613/12 NSFC Ref. : 21261160487
(please insert ref. above)

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

(Please attach a copy of the completion report submitted to the NSFC by the Mainland researcher)

Part A: The Project and Investigator(s)

1. Project Title

Study of structure, interface and property modification of metal-cluster-decorated graphitic nanostructures

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

	Hong Kong Team	Mainland Team
Name of Principal Investigator *(with title)*	Prof. Ning Wang	Prof. D.S. Su
Post	Professor	Professor
Unit / Department / Institution	Physics Department, the Hong Kong University of Science and Technology	Institute for Metal Research, Chinese Academy of Science
Contact Information	Email:phwang@ust.hk	Email: dssu@imr.ac.cn
Co-investigator(s) *(with title and institution)*	N/A	N/A

3. Project Duration

	Original	Revised	Date of RGC/ Institution Approval *(must be quoted)*
Project Start date	01/01/2013		N/A
Project Completion date	31/12/2016		N/A
Duration *(in month)*	48		
Deadline for submission of Joint Completion Report	31/12/2017		

Part B: The Completion Report

5. Project Objectives

5.1 Objectives as per original application

1. In-situ study and understand the surface/interface structure of metal-cluster-decorated graphitic nanomaterials, in particular the interaction between metal clusters and graphitic nanostructures under different catalytic reaction (e.g., hydrogenation and CO oxidation) conditions.

2. Investigate the structure and property modification of the graphitic nanostructures doped by B, N, O and P and the underlying mechanisms.

3. Elucidate the relationship between structure and property enhancement for chemically doped and metal-cluster-decorated graphitic nanostructures.

4. Combine the expertise of the two nanomaterials research teams at HKUST and IMR to contribute toward the important tasks in the study of metal clusters/graphitic nano-composite materials for potential application in catalysis.

5.2 Revised Objectives

Date of approval from the RGC: N/A

Reasons for the change: _____

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6. Research Outcome

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

1. Fast synthesis of monolayer/few-layer graphite by rapid thermal treatment (Nanoscale, (2016) 8, 2594). We developed a simple rapid thermal treatment (RTT) method for the fast and direct growth of high-quality, large-scale monolayer/few-layer graphite on SiO2/Si substrates from solid carbon sources which are stable and useful for metal cluster supports for catalytic reactions.

2. Detection of interlayer interaction in few-layer graphene (Phys. Rev. B 92(2015) 075408). We demonstrated direct evidence of the surface relaxation phenomenon in few-layer graphene. Traditionally, the van der Waals interaction/interface between the carbon layers is thought to be insignificant. However, we suggest that the interlayer or interface interaction is an important factor in explaining experimental results, and the symmetry-breaking effects in graphene sublattice should not be negligible.

3. A new method developed for fabrication of carbon nanotubes with Pd nanoparticles uniformly embedded in the inner carbon surfaces. This Pd/C nanocomposite has a high recyclability in a liquid-phase Suzuki coupling reaction. This method can be extended as a general approach to prepare metal nanoparticles supported on carbon-nanotubes. The unique micro-structures of the Pd/C nanocomposite were systematically studied by high-resolution electron microscopy (CHEMCATCHEM 6 (2014) 2600; ANGEWANDTE CHEMIE-INTERNATIONAL EDITION 53 (2014) 2634).

4. Reduction of nitrobenzene catalyzed by carbon materials (Chinese Journal of Catalysis 35 (2014) 201403033). We first characterized the nano carbon structure and N2 adsorption-desorption. We evidenced that carbon was an efficient catalyst for nitrobenzene reduction. The carbonyl group played an important role, while the carboxylic group and anhydride adversely affected the reaction.

5. Defect states in single-layer graphene decorated by Ag clusters (Scientific Reports 3(2013)2041), metal oxide and /or OH resonant impurities (APPLIED PHYSICS LETTERS 102, 203103 (2013)). We demonstrated that single-layer graphene decorated with a high density of Ag adatoms or clusters displays unconventional phenomenon of negative quantum capacitance. The Ag adatoms/clusters act as resonant impurities and form nearly dispersionless resonant impurity bands near the charge neutrality point. Resonant impurities quench the kinetic energy and drive the electrons to the Coulomb energy dominated regime with negative compressibility. We uncovered the interaction effects between resonant states (hydrogen and OH introduced by in-situ electron beam irradiation) and Landau levels by varying the applied magnetic field. Negative compressibility was detected in graphene/black phosphorus interfaces (PHYS. REV. B 93, 035455 (2016)). The interaction mechanisms and enhancement of the negative compressibility in disordered graphene were proposed.

6. Electronic properties of mono/few-layer graphite modulated by metal oxides. In addition to above metal impurity effects, we also found that metal oxides, such as Y2O3 and ZnO largely modify the properties of mono/few-layer graphite. We determined the electronic property modification of single/few-layer graphite by ultrathin Y2O3 (Nanoscale, (2013), 5, 1116). We concluded based on both DC transport and AC capacitance measurements that the broadening of Landau levels was mainly due to the additional charged impurities and inhomogeneity of carriers induced by Y2O3 ultrathin layers. We probed an efficient charge transfer between ZnO quantum dots and graphene which involve oxygen molecules from air. The electrical response of the ZnO/graphene devices to UV light and photoconductive gain was thus greatly enhanced (Small. (2013) 9(18), 3031-6).

   All these property modification effects on nano-carbon structures are important and very useful for understanding their functions in chemical sensing and catalytic reactions.

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

Through this collaborative research, both teams from HKUST and IMR have gained valuable knowledge and experience on fabricating and controlling the microstructures of nano-carbon decorated with metal clusters or metal oxide clusters. Some of these nano composites show promising properties for chemical catalytic reactions. We plan to continue our collaboration research along the same direction, particularly in the study of dynamic process of single atom catalysts and their stability using the newly installed super-resolution scanning transmission electron microscope at HK UST. A research proposal targeting on the stability of single-atom catalysts supported on atomically-thin layered structures has been submitted to the Research Grants Council (RGC) of Hong Kong.

7. The Layman's Summary

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

Having high aspect ratios, huge surface areas and high thermal stability, graphitic nanostructures containing atomic metal clusters are promising materials for chemical

sensing and catalytic reactions. The outcome of this collaborative research provided knowledges for better understanding (1) the structurally or chemically induced defects in metal cluster decorated nano-carbon structures; (2) the metal-carbon interaction; and (3) the electrical and chemical property modification of graphitic nanostructures by metal clusters and other chemical dopants. We have obtained valuable experimental data for elucidating the relationship between structure and property modification for metal-cluster-decorated and element-doped graphitic nanostructures. The results are highly relevant to fabricating efficient nano-graphitic composites for technological applications in chemical sensing and catalytic reactions.

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)*						
2013				Guo W, Xu S, Wu Z, Wang N, Loy MM, Du S*.	"Oxygen-Assisted Charge Transfer Between ZnO Quantum Dots and Graphene", Small. (2013) 9(18), 3031-6.	2013	N	Y	Y
2013				X. L. Chen, L. Wang, W. Li, Y. Wang, Y. H. He, Z. F. Wu, Y. Han, M. W. Zhang, W. Xiong, and N. Wang*	"Negative compressibility observed in graphene containing resonant impurities", APPLIED PHYSICS LETTERS 102, 203103 (2013).	2013	N	Y	Y

2013				Lin Wang, Yang Wang, Xiaolong Chen, Wei Zhu, Chao Zhu, Zefei Wu, Yu Han, Mingwei Zhang, Wei Li, Yuheng He, Wei Xiong, Kam Tuen Law, Dangsheng Su & Ning Wang*	"Negative Quantum Capacitance Induced by Midgap States in Single-layer Graphene", Scientific Reports 3(2013)2041.	2013	N	Y	Y
2013				Xiaolong Chen, Lin Wang, Wei Li, Yang Wang, Zefei Wu, Mingwei Zhang, Yu Han, Yuheng He, and Ning Wang*	"Electron-Electron Interactions in Monolayer Graphene Quantum Capacitors", Nano research. v. 6, (8), 2013, p. 619-626.	2013	N	Y	N
2013				Lin Wang, Xiaolong Chen, Yang Wang, Zefei Wu, Wei Li, Yu Han, Mingwei Zhang, Yuheng He, Chao Zhu, Kwok Kwong Fung and Ning Wang*	"Modification of electronic properties of top-gated graphene devices by ultrathin yttrium-oxide dielectric layers", Nanoscale, (2013), 5, 1116.	2013	N	Y	N
2014				Shuchang Wu, Guodong Wen, Xianmo Gu, Bingsen Zhang, Bingwei Zhong, Ning Wang and Dang Sheng Su*	"Reduction of nitrobenzene catalyzed by carbon materials", Chinese Journal of Catalysis 35 (2014) 201403033 - 3.	2014	N	Y	Y

2014				Yang Wang, Xiaolong Chen, Weiguang Ye, Zefei Wu, Yu Han, Tianyi Han, Yuheng He, Yuan Cai, and Ning Wang*	"Side-gate modulation effects on high-quality BN-Graphene-BN nanoribbon capacitors", Applied Physics Letters: 105, 243507 (2014).	2014	N	Y	Y
2014				Zefei Wu,Yu Han, Rui Huang, Xiaolong Chen, Yanqing Guo, Yuheng He, Wei Li, Yuan Cai and Ning Wang*	"Semimetallic-to-metallic transition and mobility enhancement enabled by reversible iodine doping of graphene", Nanoscale, 2014, 6, 13196.	2014	N	Y	N
2014				Lin Wang, Xiaolong Chen, Wei Zhu, Yang Wang, Chao Zhu, Zefei Wu, Yu Han, Mingwei Zhang, Wei Li, Yuheng He, and Ning Wang*	"Detection of resonant impurities in graphene by quantum capacitance measurement" PHYSICAL REVIEW B 89, 075410 (2014).	2014	N	Y	Y

2014				H.Y. Liu, L.Y. Zhang, N. Wang, D.S. Su*	"Palladium Nanoparticles Embedded in the Inner Surfaces of Carbon Nanotubes: Synthesis, Catalytic Activity, and Sinter Resistance", ANGEWANDTE CHEMIE-INTERNATIONAL EDITION 53 (2014) 2634-12638.	2014	N	Y	Y
2014				L.Y. Zhang, G.D. Wen, H.Y. Liu, N. Wang, D.S. Su*	"Preparation of Palladium Catalysts Supported on Carbon Nanotubes by an Electrostatic Adsorption Method", CHEMCATCHEM Volume: 6 (2014) 2600-2606.	2014	N	Y	N
2015				Yu Han, Zefei Wu, Shuigang Xu, Xiaolong Chen, Lin Wang, Yang Wang, Wei Xiong, Tianyi Han, Weiguang Ye, Jiangxiazi Lin, Yuan Cai, K. M. Ho, Yuheng He, Dangsheng Su, Ning Wang*	"Probing defect-induced midgap states in MoS2 through graphene-MoS2 heterostructures", Advanced Materials Interfaces 2 (2015) 1500064.	2017	Y	Y	N

2015				Zefei Wu, Yu Han,Wei Zhu, Mingquan He, Shuigang Xu, Xiaolong Chen, Weiguang Ye, Tianyi Han, Huanhuan Lu, Rui Huang, Lin Wang, Yuheng He, Yuan Cai, Rolf Lortz, Ning Wang*	"Detection of Interlayer Interaction in Few-layer Graphene", Phys. Rev. B 92 (2015) 075408.	2017	Y	Y	Y
2016				Z.F. Wu, Y.Q. Guo, Y.Z. Guo, R. Huang, S.G. Xu, J. Song, H.H. Lu, Z.X. Lin, Y. Han, H.L. Li, T.Y. Han, J. Lin, Y.Y. Wu, G. Long, Y. Cai, C. Cheng, D.S. Su, J. Robertsonc and Ning Wang*	"A fast transfer-free synthesis of high-quality monolayer graphene on insulating substrates by a simple rapid thermal treatment", Nanoscale, (2016), 8, 2594.	2017	Y	Y	N
2016				Y.Y. Wu, X.L. Chen, Z.F. Wu, S.G. Xu, T.Y. Han, J. Lin, B. Skinner, Y. Cai, Y.H. He, C. Cheng, and N. Wang*	"Negative compressibility in graphene-terminated black phosphorus heterostructures", PHYSICAL REVIEW B 93, 035455 (2016).	2017	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)*
August/2013 /Hailar	Resonant impurities and negative quantum capacitance in single-layer graphene	9th Cross-Strait Workshop on "Nano Science and Technology"	2013	No	Yes
December/2 013/Hong Kong	Disorder and resonant states in single layer graphene detected by quantum capacitance measurement.	Interdisciplinary Nanoscience for Energy, Life and Environment (INELE2013)	2013	No	Yes
December/2 014/Hong Kong	Probing the electron states and metal-insulator transition mechanisms in atomically thin MoS2.	11th Cross-Strait Workshop on "Nano Science and Technology"	2014	Yes	Yes
July/2015/Si ngapore	Dimension-controlled synthesis of ZnO nanostructures and their novel properties for potential applications.	ICMAT2015 & IUMRS-ICA2015, Materials Research Society, Singapore	2015	Yes	Yes

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
Z.F. Wu	PhD in Physics	01/09/2010	August 2014
Y. Han	PhD in Physics	01/09/2011	August 2015
Y.Y. Wu	M. Phil. in Physics	01/09/2014	June 2016

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

No.