CNMS USE ONLY
Proposal Number: CNMS2012-270
Date Received: 5/2/12

CENTER FOR NANOPHASE MATERIALS SCIENCES RESEARCH PROPOSAL

Submit complete proposal package to: CNMS User Coordinator, Oak Ridge National Laboratory, Email: cnmsuser@ornl.gov
Your proposal package must include:
(1) Completed proposal form;
(2) Two-page NSF-style CV for the Principal Investigator only; and
(3) Supplementary appendix for use of microanalysis facilities provided by SHaRE (if applicable).

Title of Proposal:	Date Submitted:
Real-time characterization and control of graphene growth kinetics by pulsed CVD	5/2/12

Principal Investigator - Responsible for progress of the project and primary point of contact for all correspondence from CNMS.

Name of PI: Prof. I. M. Smart	☒ Check if PI will participate on-site at ORNL
Institution: Your University	Phone: 123-456-7890
Dept: Materials Science & Engineering	Fax: 123-456-8907
Street Address or P.O. Box: PO Box 20001	Email: im-smart@youruniv.edu
City University City State/Prov. TN Country USA Postal Code 91111	Citizenship: US

Collaborators - List everyone who will participate in this project, including students, postdocs, etc.
Only participants named below will be eligible for an ORNL badge authorized through this project.

Name of Collaborator (attach additional sheets if necessary)	**Institution and Address**	**Citizen-ship**	**Email**	**Please Check If Participating On-Site**
A. Grad Student	MS&E Dept., Campus Box 4444 Your University University City, TN 91111	Greece	a.grad@youruniv.edu	☒
Prof. A. Colleague	Dept of Chemical Eng. PO Box 3333 Another College College Town, NY 92221	USA	a. colleague@acoll.edu	☒
Postgrad U. Fellow	MS&E Dept., Campus Box 4444 Your University University City, TN 97111	UK	post.fell@youruniv.edu	☐
				☐
				☐
				☐

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CNMS Facilities Requested

Indicate below the facilities and the number of days for each at CNMS that will be required for this project. The Research Description section must describe how each of the selected facilities will be used, including estimates of the quantities of materials/samples to be synthesized or characterized and the estimated time required in each facility. Users are encouraged to contact CNMS staff for assistance in estimating the appropriate times and quantities. See http://www.cnms.ornl.gov/capabilities/cap.shtml for detailed descriptions of these facilities and list of contacts.

NANOMATERIALS SYNTHESIS AND FUNCTIONAL ASSEMBLY

MACROMOLECULAR NANOMATERIALS

- ☐ ____ Polymer synthesis (Anionic, radical, cationic, and step growth polymerizations; composite materials)
- ☐ ____ Synthesis of novel monomers and precursors
- ☐ ____ Deuterated monomers, polymers, and specialty molecules
- ☐ ____ 500 MHz Solution NMR Spectroscopy
- ☐ ____ Macromolecular characterization- molecular weight, spectroscopy, scattering, thermal analysis (details on web site)
- ☐ ____ Other: specify

OPTOELECTRONIC NANOSTRUCTURES

- ☐ ____ Synthesis of SWNT's, NT Arrays, graphene & 2D materials, NW's, NP's, or thin films by CVD, Laser Vaporization, & PLD with in situ diagnostics
- ☐ ____ Complex oxide heterostructure PLD w/ high-pressure RHEED, RF Sputtering and Laser Heating
- ☒ 5 Laser/nanomaterial processing
- ☒ 5 Wet/dry assembly of organic/inorganic/metal heterostructures including dual glove box evaporator system and/or sonospray deposition system
- ☐ ____ Electrical Characterization
- ☐ ____ Optoelectronic Characterization (including PV and OLED efficiency measurements, and AC Impedance)
- ☒ 30 Laser-based spectroscopy (ultrafast, tunable micro/macro Raman, etc.)
- ☐ ____ Spectroelectrochemistry
- ☐ ____ Other: specify

CATALYTIC NANOSTRUCTURES

- ☐ ____ Synthesis: porous materials, nanoparticles, sol-gel, hydrothermal, ALD and solid state synthesis
- ☐ ____ Structural characterization of surface & bulk catalytic nanomaterials (including Raman scattering, volumetric gas adsorption, TG-MS, CHNS/O analysis, etc.)
- ☐ ____ Catalyst performance characterization (reactivity, temperature programmed response, transient catalytic reactors with FTIR/Raman)
- ☐ ____ Battery cycler, frequency response analyzer, potentiostat, and glove boxes for battery cell assembly
- ☐ ____ Other: specify

NANOMATERIALS THEORY INSTITUTE

- ☐ CPU hours NTI Computational Cluster, capacity computing
- ☐ CPU hours Facilitation of access to NERSC, high-performance
- ☐ CPU hours Facilitation of access to NCCS, leadership class
- ☐ ____ NTI staff support, experimental project
- ☐ ____ NTI staff support, theoretical project
- ☐ ____ Other: specify

IMAGING AND NANOSCALE CHARACTERIZATION

- ☐ ____ Advanced SPM: air, liquid (cAFM, PFM, ESM, MFM)
- ☐ ____ Advanced SPM: glove box
- ☐ ____ AFM: topography
- ☐ ____ Laser MBE with in situ RHEED, AFM/STM, electron spectroscopies
- ☐ ____ Magnetic Property Measurement System
- ☐ ____ SEMPA
- ☐ ____ Ultrahigh Vacuum 4-probe STM
- ☐ ____ Ultrahigh Vacuum AFM
- ☐ ____ Ultrahigh Vacuum STM/STS
- ☐ ____ Other: specify

NANOFABRICATION RESEARCH LABORATORY

- ☐ ____ Process Design for Cleanroom Processes
- ☐ ____ E-beam Lithography
- ☐ ____ Dual-beam SEM/FIB
- ☐ ____ FirstNano Rapid Thermal Processing Tool
- ☐ ____ Plasma Atomic Layer Deposition
- ☐ ____ General Cleanroom Use (see website for details)
- ☐ ____ Helium-Ion Milling (Zeiss Orion NanoFab)
- ☐ ____ Other: specify

BIO-INSPIRED NANOMATERIALS

- ☐ ____ Multimodality live-cell imaging
- ☐ ____ DC-PECVD synthesis of VACNFs

MICROSCOPY, NEUTRON, and X-RAY SCATTERING

- ☒ 5 Advanced SEM (Zeiss Merlin)
- ☐ ____ Soft Matter TEM (Zeiss Libra)
- ☐ ____ High-resolution TEM/STEM with EELS & EDS (Hitachi HF3300)
- ☒ 3 Low-voltage (60-100kV) aberration-corrected STEM/EELS (Nion U100)
- ☒ 3 300kV aberration-corrected STEM/EELS (FEI Titan S)
- ☒ 1 TEM Specimen Preparation (FIB, microtome, ion mill)
- ☐ ____ Atom Probe Tomography (LEAP 4000X HR)
- ☐ ____ FIB to prepare APT needles (FEI Nova 200)
- ☐ ____ Helium-Ion Microscopy (Zeiss Orion NanoFab)
- ☐ ____ X-ray diffraction and small-angle scattering
- ☐ Neutron Scattering - attach Neutron Scattering appx.
- ☐ ____ Other: specify

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Scheduling Considerations

Estimate the total number of days that will be spent at the CNMS: 30 (Required)
Propose a specific date to begin work at CNMS: (Optional)

Samples and Identification of Hazards

Research samples used in this project will be:

- ☒ Synthesized at CNMS
- ☐ Supplied by user with additional processing at CNMS
- ☐ Wholly supplied by user, only characterized at CNMS
- ☐ I have special sample handling requirements (e.g., air- or light-sensitive materials, etc.) (specify):

Provide a brief description of ALL materials (samples, supplies, and equipment) that you plan to bring to CNMS. Materials and equipment that are not specifically listed here will not be allowed into CNMS. Include common name and chemical formula if applicable. Check any boxes below that apply to these materials.

☐ No major safety issues	☐ Corrosive Material*	☐ Toxic Material*	☐ Electrical/Electronic Equipment
☐ Flammable Material*	☐ Radioactive Material*	☐ Explosive Material*	☐ Cryogenic hazard
☐ Carcinogenic*	☐ Biohazardous*	☒ Lasers	☐ High Pressure

☐ Other*: specify

User Access Mode: ☒ General User ☐ Partner User (for development of specialized facilities or methods)
(*For definitions of User Access Modes see* http://cnms.ornl.gov/user/policies.shtm#modes)

State in your own words the reasons that led you to propose performing this research at the CNMS as opposed to some other facility, i.e., why are CNMS facilities or expertise needed? (limit to 2 lines).
Tunable Raman system is required

Have you contacted a CNMS staff member to discuss the feasibility of your project? ☒ Yes ☐ No
Contact Name(s): Dave Geohegan

Please Categorize Your Proposal (Required for DOE reporting purposes)

Subject of this Project (check all that apply)		**Sources of Support (check all that apply)**
☒ Materials Sciences (including condensed matter physics, materials chemistry)	☐ Earth Sciences	☒ DOE, Basic Energy Sciences
☐ Physics (excluding condensed matter physics)	☐ Environmental Sciences	☐ DOE, Biological & Environmental Res.
☐ Chemistry (excluding materials chemistry)	☐ Optics	☐ DOE, Other: specify
☐ Polymers	☐ Engineering	☐ DOD: specify
☐ Medical Applications	☐ Instrumentation or technique development related to user facilities	☐ NSF
☐ Biological, Life Sciences (excluding medical applications)	☐ Purchase of specialty services or materials	☐ NIH
	☐ Other: specify	☐ NASA
		☐ USDA
		☐ Other US Govt: specify
		☐ Industry
		☐ Foreign: specify
		☐ Other: specify

Status of Funding for Proposed Research

Occasionally, an approved CNMS user may not be able to utilize their full time allocation because they do not have sufficient funding in place. The information requested below will be used only to help us anticipate how much potential unclaimed time may become available to support additional user projects. It will not affect the outcome of the review process. Please check the box that applies.

☒ Proposal team members have research grant(s) already in place that is/are sufficient to support their participation in this project.
☐ We have submitted proposal(s) to the following agencies to request funding that will be needed to support our participation:
Funding agency _____; Expected decision date _____

SUGGESTED REVIEWERS (Optional) – You may suggest up to 5 of the most suitable reviewers from the current CNMS Proposal Review Committee listed at http://www.cnms.ornl.gov/about_cnms/PRC.shtm. In addition, you may also list up to 3 individuals who are not on the CNMS Review Committee. Do not include anyone affiliated with ORNL, CNMS, or your home institution, recent collaborators, or anyone else who may have "Potentially Disqualifying Conflicts of Interest" as defined by the *National Science Foundation*, (see http://www.nsf.gov/pubs/gpg/nsf04_23/appb.jsp).

From the CNMS Proposal Review Committee:
1. Prof. Apparao Rao 2. Prof. Andrew Rinzler 3. Prof. Liming Dai
4. _____ 5. _____

Optional- Additional reviewers NOT from the CNMS Review Committee (provide institutional affiliation):
6. Name: _____ Institution _____
7. Name: _____ Institution _____
8. Name: _____ Institution _____

Optional- Please EXCLUDE the following members of the CNMS Proposal Review Committee due to a potential conflict of interest: Prof. Gerd Duscher is a member of the research team

PRINCIPAL INVESTIGATOR'S AGREEMENT: *Signature is not required if the proposal is transmitted by email from the PI.*

By signing or by electronic submission, I certify that the information provided herein is correct to the best of my knowledge and that I intend to publish the results of this research. I also agree to (1) acknowledge the CNMS in all publications resulting from the use of the facility; (2) send a timely draft of all manuscripts to all ORNL co-authors for review prior to submission; and (3) send a copy of resulting publications to the CNMS User Coordinator.

Signature of PI: _____ **Printed Name:** I. M. Smart **Date:** 5/1/12

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DESCRIPTION OF PROPOSED RESEARCH

The description must be limited to a maximum of 2 pages, including text and figures. PIs are encouraged to consult the CNMS Proposal Evaluation Guidelines used by reviewers at http://www.cnms.ornl.gov/about_cnms/eval_guidelines.shtm.

Note: If you plan to use figures, it is best to copy/paste pre-formatted figures with text into this form.

ADDRESS EACH OF THE FOLLOWING QUESTIONS IN A SEPARATE SECTION.

A maximum of 2 pages can be used to respond to the 6 questions below; Proposers may determine the amount of space used for each question.

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1) **What is/are the main scientific question(s) that you plan to address?**

The unique thermal, electrical, and optical properties of graphene[1] may enable many potential applications involving this material, especially in the area of nanoelectronics[2]. Among the many different methods of graphene synthesis, chemical vapor deposition (CVD) is the most attractive since it allows one to grow graphene on metal catalyst (e.g, Cu, Ni) patterned substrates.[3] The majority of the recent studies are limited to simple empirical optimization of the CVD growth parameters. However, the growth mechanism of graphene is not very well-understood, thereby hindering the understanding required for potential applications and the major challenges are: (1) Control nucleation density and number of layers, (2) Rapid growth over large areas ("supergrowth?"), and (3) Growth of large, single-crystalline grains.

An important question that is directly related to the discovery of new synthesis methods is whether graphene grows isothermally[4], i.e., at the growth temperature, as it occurs in the case of catalyst-assisted carbon nanotube growth, or upon cooling[5,6]? Surprisingly, the majority of published studies on Ni-CVD graphene growth are based on the premise that growth occurs during cool-down after deposition assuming dissolution precipitation mechanism, with no strong experimental evidence for such a view. Another question relates directly to the primary building blocks for graphene growth: does it grow from carbon atoms through the dissolution-precipitation mechanism, carbon clusters, or more complex intermediates through pure chemical assembly? Also, it is important to understand how fast graphene can be grown. Typically, it takes minutes to grow graphene on Ni and Cu. Can one grow graphene faster and what factors limit the growth rate? Considering that CVD growth of graphene is remarkably similar to that of carbon nanotubes - i.e., cap formation on a metal nanoparticle during the initial stages of nanotube growth is much like graphene growth on metal surfaces - our pulsed CVD approach (Fig.1a,b) developed for real-time studies of nanotube growth[7-9] can be applied directly to monitor and control graphene growth. For example, mounting evidence from our *in situ* diagnostics studies of nanotube growth indicate that the initial stages of carbon nanotube growth include a flux dependent induction time[8] (Fig. 1c), which can be described by autocatalytic kinetics, and begs the question: can the same kinetics describe the initial stages of graphene growth? **Here we propose** to perform UV-Raman spectroscopy at high temperatures at the CNMS in conjunction with our pulsed CVD approach to explore the role of feedstock flux in driving the growth kinetics of graphene.

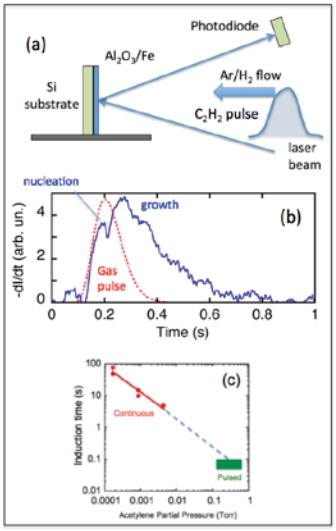

Fig. 1. (a) Pulsed CVD approach to probe nanotube growth kinetics. (b) Fast kinetics of SWNT nucleation and growth measured *in situ*. (c) C_2H_2 flux driven kinetics of SWNT growth [7-9]

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2) **Outline the overall technical approach that you plan to use to address the above questions. This section should provide the context for research tasks described below in sections (3), home institution activities, and (4), CNMS research.**

To understand how graphene grows on "catalytic" metal films such as Ni - i.e., isothermally at the growth temperature or during cool down - and to explore its growth kinetics, we have proposed to combine pulsed CVD and several *in situ* optical diagnostics techniques, namely Raman scattering, direct optical imaging, and time-resolved reflectivity. Pulsed CVD approach will allow us to grow graphene incrementally, to limit the time available for nucleation and growth, and to measure transient nucleation and growth kinetics. In this proposal we'll focus on the use of *in situ* UV-confocal micro-Raman spectroscopy to explore the growth of graphene using well-defined pulses of hydrocarbon gas to understand growth mechanisms and kinetics.

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3) **What research tasks will be carried out at the users' home institution or elsewhere outside of the CNMS? Include any preliminary syntheses, measurements, or tests that have been/will be performed in preparation for the proposed research at the CNMS.**

We'll provide a modified microscope Linkam stage (TS1500), which is capable to operate at low gas pressures required for this study.

4) **Describe very clearly and specifically the research tasks to be carried out at the CNMS and the expected outcomes from the CNMS tasks. Include any technical milestones that must be met for the research to be successful.** (This should be the longest and most detailed section in the proposal)

In this proposal we will focus mainly on the following two research tasks.

1. Feedstock flux dependence of graphene growth mode and kinetics.

To grow graphene we'll use a high temperature microscope stage (Linkam TS1500), which is modified to operate at low gas pressures. Some of the metal catalyst films will be deposited at CNMS using the Controlled Atmosphere Dual Glove Box Evaporateor System. C_2H_2 gas pulses (ms-durations) will be ejected into the fast flow of Ar/H_2 through the microscope Linkam stage using a pulsed valve and graphene growth will be monitored *in situ* using Raman scattering. In the proposed experiments the Raman measurements will be conducted at high temperatures (700-900 C). Therefore, the black body radiation background is a big issue in these measurements. To minimize the blackbody radiation background in the Raman spectra during *in situ* monitoring of graphene growth at the elevated temperatures, we plan to use UV laser excitation (provided by Tunable Raman system at CNMS), which gives a small background. We expect that, similar to SWNT growth, both surface-growth and dissolution/precipitation can exist under certain circumstances. To determine if there is a clear crossover point or region, we will explore the feedstock flux dependence in selectively driving surface growth processes using pulsed CVD and *in situ* Raman scattering measurements. Using this approach we expect to find the conditions for fast surface driven growth of graphene and understand its growth kinetics at different growth regimes.

2. Kinetics of layer formation and evolution during graphene growth.

For some applications graphene with the specific number of layers is required. Therefore it is important to understand how the layers are forming during graphene growth. We propose to addres this problem using *in situ* UV Raman scattering measurements through simultaneous detection of the G- and 2D-Raman bands. This real time measurements of the 2D/G ratio, which is directly related to the number of graphene layers (in the case of a few layer graphene) will allowed us to understand the mechanism and kinetics of graphene layer formation. Using this approach we'll be able to answer the questions if it is possible to control the number of layers using for example short pulses of a feedstock gas.

5) **Provide an overall timeline for the CNMS tasks and describe how each facility/instrument that is checked on p. 2 will be used, including estimates of the number/quantities of samples, instrument time, CPU time, etc.**

Each of the two tasks outlined above will require 15 days of the tunable Raman system time. The total required time is 30 days. In addition, approximately 10-15 samples should be analysed using SEM and 3-4 samples using aberration corrected microscopy at the ShaRE facility. To prepare graphene samples for TEM measurements we also will need laser processing facility to perform graphene cleaning after it transfer to a TEM grid.

6) **What is your team's specific experience and expertise relevant to this research project?**

Recently, we have developed methods to study the response of catalytically active surfaces to instantaneously changing source gas flux in a form of well defined pulses. The key feature of this pulsed CVD method is the use of real-time diagnostics based on time-resolved reflectivity (TRR) of a laser beam from the catalyst-coated substrate sampled at 200 Hz. Detailed computational models of the gas pulse evolution were developed to extract the kinetics of carbon nanostructure growth.[7-9] Here we propose to use similar approaches to understand the growth mechanisms of graphene.

LITERATURE CITED ABOVE - if any (not included in the 2 page limit)

[1] Novoselov, K. S., Nobel Lecture: Graphene: Materials in the Flatland. *Rev Mod Phys* **2011,** *83* (3), 837-849.

[2] Rummeli, M. H.; Rocha, C. G.; Ortmann, F.; Ibrahim, I.; Sevincli, H.; Borrnert, F.; Kunstmann, J.; Bachmatiuk, A.; Potschke, M.; Shiraishi, M.; Meyyappan, M.; Buchner, B.; Roche, S.; Cuniberti, G., Graphene: Piecing it Together. *Adv Mater* **2011,** *23* (39), 4471-4490.

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[3] Safron, N. S.; Kim, M.; Gopalan, P.; Arnold, M. S., Barrier-Guided Growth of Micro- and Nano-Structured Graphene. *Adv Mater* **2012,** *24* (8), 1041-1045.

[4] Weatherup, R. S.; Bayer, B. C.; Blume, R.; Ducati, C.; Baehtz, C.; Schlogl, R.; Hofmann, S., In Situ Characterization of Alloy Catalysts for Low-Temperature Graphene Growth. *Nano Lett.* **2011,** *11* (10), 4154-4160.

[5] Li, X. S.; Cai, W. W.; Colombo, L.; Ruoff, R. S., Evolution of Graphene Growth on Ni and Cu by Carbon Isotope Labeling. *Nano Lett.* **2009,** *9* (12), 4268-4272.

[6] Reina, A.; Jia, X. T.; Ho, J.; Nezich, D.; Son, H. B.; Bulovic, V.; Dresselhaus, M. S.; Kong, J., Large Area, Few-Layer Graphene Films on Arbitrary Substrates by Chemical Vapor Deposition. *Nano Lett.* **2009,** *9* (1), 30-35.

[7] A. A. Puretzky, D. B. Geohegan, J. J. Jackson, S. Pannala, G. Eres, C. M. Rouleau, K. L. More, N. Thonnard, and J. D. Readle, Incremental growth of short SWNT arrays by pulsed chemical vapor deposition, *Small (2012) published online DOI: 10.1002/smll.201102173.*

[8] D. B. Geohegan, A. A. Puretzky, J. J. Jackson, C. M. Rouleau, G. Eres, and K. L. More, Flux-Dependent Growth Kinetics and Diameter Selectivity in Single-Wall Carbon Nanotube Arrays, *ACS Nano* **5** (10), 8311 (2011).

[9] J. J. Jackson, A. A. Puretzky, K. L. More, C. M. Rouleau, G. Eres, and D. B. Geohegan, Pulsed Growth of Vertically Aligned Nanotube Arrays with Variable Density, *ACS Nano* **4**(12), 7573 (2010).

The section below is for PARTNER USER proposals only (half page or less - not included in the 2 page limit)

PARTNER USER proposals only: What unique, new capabilities will be developed at the CNMS as a result of this approach? How will these contribute to future research by other CNMS users?
(enter text here)

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