OAK RIDGE National Laboratory | CENTER FOR NANOPHASE MATERIALS SCIENCES

CNMS USE ONLY
Proposal Number: NEW
Date Received:

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 CV (NSF-style or similar) for the Principal Investigator only; and
(3) Appendix for use of neutron scattering at the SNS or HFIR (if applicable).
Do not include any proprietary or sensitive information in your proposal.

Title of Proposal:	Date Submitted:
Real-time characterization and control of graphene growth kinetics by pulsed CVD	5/2/2018

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/Employer: Your University	Phone: 123-456-7890
Dept: Materials Science & Engineering	Fax: 123-456-7890
Street Address or P.O. Box:PO Box 20001	Email: im-smart@youruniv.edu
City University City State/Prov. Tn Country USA Postal Code 9111	

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

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

Next to each CNMS facility below that you plan to use, indicate the number of days that you are requesting. **NOTE: CNMS reserves the right to refuse access to any facility that is not marked on this page.** 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.

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

CHARACTERIZATION

____ 500 MHz Solution NMR Spectroscopy
____ Macromolecular characterization- molecular weight, spectroscopy, scattering, thermal analysis, MALDI-TOF, broadband dielectric spectroscopy (details on website)
____ Thin Film Characterization- ellipsometry, FTIR-ATR, FTIR microscopy, contact angle goniometer (details on website)

FUNCTIONAL HYBRID NANOMATERIALS

____ Synthesis of Nanomaterials by CVD, PLD with in situ diagnostics – 2D TMCs, graphene; 1D SWNTs, NT Arrays, NWs; NPs, SWNHs
____ Oxide Thin Film PLD with high-pressure RHEED – films, complex heterostructures, PLD with RF sputtering and laser heating
5 Laser Material Interactions and Processing with in situ diagnostics – heating, patterning, thinning, structuring, transfer, with XY scanning
5 Wet/Dry Assembly of Organic/Inorganic/Hybrid Films and Devices – dual glovebox evaporator, Sonospray, 2D stamping, perovskite PV

CHARACTERIZATION

30 Optical Characterization and Laser Spectroscopy – ultrafast dynamics, microRaman, PL lifetime, UV-VIS-NIR, fluorometry, PLE
____ Electrical/Optoelectronic Characterization in Controlled Environments – Sensors, R-T, AC impedance, PV and OLED efficiency (details on website)
____ Physical Property Measurement System (PPMS)
____ Catalysis and *Operando* Spectroscopy: gas phase, electro- and photo-chemistry

NANOMATERIALS THEORY INSTITUTE

____ K cpu-hours NTI Computational Cluster, capacity computing
____ K cpu-hours Facilitation of access to NERSC, high-performance
____ K cpu-hours Facilitation of access to NCCS, leadership class
____ days NTI staff support, experimental project
____ days NTI staff support, theoretical project

NEUTRON SCATTERING & X-RAY CAPABILITIES

____ X-ray diffraction and small-angle scattering
____ Neutron Scattering - attach Neutron Scattering appx.

SCANNING PROBE MICROSCOPY

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

NANOFABRICATION RESEARCH LABORATORY

____ Process Design for Cleanroom Processes
____ E-beam Lithography
____ Dual-beam SEM/FIB
____ 3D Direct-Write Fabrication
____ FirstNano Rapid Thermal Processing Tool
____ Plasma Atomic Layer Deposition
____ Helium-Ion Milling, Microscopy, Imaging (Zeiss Orion)
____ General Cleanroom Use (see website for details)

CHEMICAL IMAGING

____ AFM/FIB-ToF-SIMS
____ Helium-Ion Microscope with SIMS
____ AFM-NanoIR2-s
____ MALDI-ToF Imaging
____ Advanced SEM with EDS (Zeiss Merlin)

BIO-INSPIRED NANOMATERIALS

____ Multimodality live-cell imaging
____ DC-PECVD synthesis of VACNFs or CNSs

ELECTRON & ATOM PROBE MICROSCOPY

3 Low-voltage (60-100kV) aberration-corrected STEM/EELS (Nion UltraSTEM)
____ Low-voltage (60-100kV) monochromated, aberration-corrected (MAC)-STEM/EELS (Nion Hermes)
3 300kV aberration-corrected STEM/EELS (FEI Titan)
1 TEM Specimen Preparation (FIB, microtome, ion mill, etc.)
____ Atom Probe Tomography (Cameca LEAP 4000X HR)
____ FIB-preparation of atom probe needles (FEI Nova200)
DISCONTINUED: Zeiss Libra & Hitachi HF3300 (details on website)
Coming soon!- JEOL NEOARM TEM/STEM- fall proposal cycle (2019A)

OTHER FACILITIES- If you have identified other facilities not listed above that you want to use, *you must first contact a CNMS Staff Member to discuss availability* then provide their name and facility description below. CNMS cannot pay any costs associated with use of other ORNL facilities.

CNMS Staff Member(s): _____ Facility Description: _____

Scheduling Considerations

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	☐ Explosive Material	☐ Electrical/Electronic Equipment
☐ Flammable Material	☐ Radioactive Material	☐ Lasers	☐ Other: specify
☐ Carcinogenic	☐ Biohazardous	☐ Cryogenic hazard	
☐ Human subjects or human bodily Materials	☐ Toxic Material	☐ High Pressure	

User Access Mode: ☒ General User ☐ Partner User (for development of specialized facilities or methods)
(*For definitions of User Access Modes see* https://www.ornl.gov/facility/cnms/subpage/proposal-types.)

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

How did you first learn about CNMS?

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

Suggestions for capabilities that CNMS may consider acquiring that would benefit your research:

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 https://www.ornl.gov/facility/cnms/subpage/proposal-review-committee. 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. Rinzler 2. Dai 3. Verduzco
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

Keywords: list a few keywords here to help in matching potential reviewers

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:** 5/2/18

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 Review Criteria for CNMS Research Proposals at https://www.ornl.gov/facility/cnms/subpage/user-policies.
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 numbered questions below; Proposers may determine the amount of space used for each question.

1) **What is/are the main scientific or technological question(s) that you plan to address?**
The unique thermal, electrical, and optical properties of graphene1 may enable many potential applications involving this material, especially in the area of nanoelectronics2. 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 isothermally4, i.e., at the growth temperature, as it occurs in the case of catalyst-assisted carbon nanotube growth, or upon cooling5,6? 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

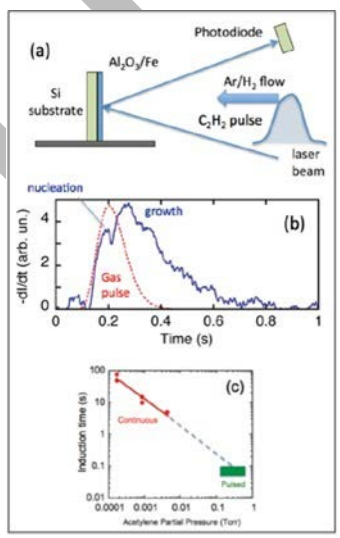

Fig. 1. (a) Pulsed CVD approach to probe nanotube growth kinetics. (b) Fast kinetics of SWNT nucleation and growth measured in situ. (c) C2H2 flux driven kinetics of SWNT growth [7-9]

- our pulsed CVD approach (Fig.1a,b) developed for real-time studies of nanotube growth7-9 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 time8 (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.

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.

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 and the need for specialized capabilities and/or expertise at the CNMS 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. C2H2 gas pulses (ms-durations) will be ejected into the fast flow of Ar/H2 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.

PUBLICATION RECORD: Have you had any previous CNMS project(s), including SHaRE? YES ___ NO _X_ (response required) If yes, list publications resulting from your past project(s) – maximum of 10: (not included in the 2 page limit)

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.

[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?