CNMS USE ONLY
Proposal Number: CNMS2007-352
Date Received: 4/14/07

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: Synthesis and reactivity studies of morphologically controlled Cerium oxide	Date Submitted: 4/14/07

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	☐
				☐
				☐
				☐

CNMS Facilities Requested

Indicate below the facilities 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.shtm for detailed descriptions of these facilities and list of contacts.

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

FUNCTIONAL NANOMATERIALS
- ☐ Laser Vaporization Synthesis of SWNTs, NWs, NPs (including in situ diagnostics)
- ☐ CVD: Thermal, molecular beam, PECVD (microwave) of CNTs, NWs, arrays (including in situ laser diagnostics)
- ☐ Oxide heterostructure PLD w/ high-pressure RHEED
- ☐ Laser/nanomaterial processing
- ☐ SWNT Purification, Functionalization, and Composites
- ☐ Electrical Characterization of nanomaterials
- ☐ Optoelectronic Characterization of nanomaterials
- ☐ Laser-based spectroscopy of nanomaterials (ultrafast, tunable micro/macro Raman, etc.)
- ☐ Spectroelectrochemistry
- ☐ Other: specify

MAGNETISM, TRANSPORT & SCANNING PROBES
- ☐ In situ MBE
- ☐ In situ laser MBE w RHEED, AFM/STM, surface characterization
- ☐ SEMPA
- ☐ Ultrahigh Vacuum Cryo 4-probe STM
- ☐ Ultrahigh Vacuum Variable Temperature AFM/STM
- ☐ AFM: topography
- ☐ Advanced SPM: air or liquid (MFM, SCM, PFM, SSPFM etc.)
- ☐ Other: specify

BIO-INSPIRED NANOMATERIALS
- ☐ Biocompatible AFM-based litho. (e.g., patterning of SAMS)
- ☐ Multimodality live-cell imaging
- ☐ PECVD (DC and RF) synthesis of VACNFs
- ☐ Chemical/Biological functionalization of nanomaterials

CATALYSIS & NANO-BUILDING BLOCKS
- ☒ Synthesis: porous materials, nanoparticles, sol-gel, hydrothermal and ALD
- ☒ Structural characterization of oxide and metal nanomaterials, surface and bulk structure (including Raman scattering, nano-zetameter,etc.)
- ☒ Catalyst performance characterization including gas and condensed phase reactivity and selectivity
- ☐ 500 MHz Liquid/Solid NMR Spectroscopy
- ☐ Other: specify

NANOFABRICATION RESEARCH LABORATORY
- ☐ Process Design
- ☐ E-beam Lithography
- ☐ Dual-beam SEM/FIB
- ☐ General Cleanroom Use (see website for details)
- ☐ Other: specify

THEORY, MODELING & SIMULATION
- ☐ NTI Computational Cluster, medium performance
- ☐ Facilitation of access to NERSC, high-performance
- ☐ Facilitation of access to NLCF, leadership class
- ☐ NTI staff support, experimental project
- ☐ NTI staff support, theoretical project
- ☐ Other: specify

NANOSCALE STRUCTURE AND DYNAMICS: NEUTRONS, ELECTRONS, AND X-RAYS
- ☐ Advanced SEM
- ☒ Z-contrast STEM
- ☒ X-ray diffraction
- ☐ X-ray fluorescence
- ☐ Shared Research Equipment- attach SHaRE appendix (aberration corrected electron microscopy, TEM or STEM/EELS; atom probe; nanoindenter)

Proposals for neutron scattering time should be submitted separately to the ORNL Neutron Science User Program. See http://neutrons.ornl.gov/users/ for instructions/schedule information.

Scheduling Considerations

Estimate the total number of days that will be needed at the CNMS: 30 (Required)

Propose a specific date to begin work at CNMS: July 1, 2007(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 into the 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*	☐ High-Voltage Electrical
☐ 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).
Expertise in hydrothermal synthesis; availlable environmental controlled DRIFTS; CNMS is simply the best user facility in the world

Have you contacted a CNMS staff member to discuss the feasibility of your project? ☒ Yes ☐ No
Contact Name(s): Peter Gunn, Sara Smile

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- Suggest a minimum of 4 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 (4 required):
1. Fabio. Ribeiro 2. Raul Lobo 3. Robert Davis (Virginia)
4. G. Lester 5. (optional) _____

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: _____

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:** 4/14/07

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?**

Cerium oxide, especially when promoted with Zr oxide, is well known to perform as an oxygen storage component in automotive catalysts. In this role, it is capable releasing lattice oxygen during oxidation of CO and hydrocarbons and of subsequently re-acquiring oxygen from oxidants such as O_2, NO or water. It is this facile exchange of lattice oxygen which is associated with the measured oxygen storage capacity of CeO_2. CO oxidation on the surface of a CeO_2 supported catalyst implies the adsorption of CO followed by transfer of O from the ceria lattice to the molecule. In spite of the simplicity of this reaction, many questions remain and an improved understanding of how the structure of cerium oxide affects the reactivity toward CO is clearly needed.

We have examined model surfaces of metal-free, highly oriented CeO_2 (111) films and these do not appear to adsorb CO [1,2]. In the presence of metal particles (e.g. Rh, Pt, Pd) there is evidence that a carbonate forms, presumably on the CeO_2, by transfer of CO from the metal. This ceria-based species apparently can not form without the metal particle. However, no CO_2 desorption product, and therefore no CO oxidation, is observed. Kinetic studies on model films of CeO_2 grown by spray pyrolysis and doped with Pt, or Pd provide evidence that water-gas shift reaction occurs by the redox mechanism [3]. In this case CO adsorbs on the metal particle and somehow extracts O from the ceria lattice implying that it must transfer onto the ceria at some point. This model catalyst has been shown to deactivate as CeO_2 particles grow, attributed to the structure dependent loss of reducibility. Although CO is assumed to adsorb on supported metal particles, there is little direct evidence of CO adsorbing or interacting with the ceria support on these model systems. In contrast, on ceria powders FTIR studies [4] indicate that CO adsorbs to form a carbonate, even without metal particles. Similarly clean CeO_2 is readily reduced by CO implying adsorption of CO without aid of the metal particles. CO oxidation catalyzed by pure, high surface area CeO_2 has been observed and the activity increases with the growth of more reactive {100} surfaces. The adsorption of CO on different surfaces of CeO_2 has also been simulated using DFT calculations which demonstrate that the interaction of CO with ceria is strongly surface structure dependent [5].

Many questions need to be addressed. How does CO interact with CeO_2 and in particular how does this interaction depend upon surface termination? On which surfaces does CO adsorb? Does CO ever adsorb as a linear carbonyl or does it form carbonate? Does desorption/decomposition of the carbonate lead to CO_2 desorption and therefore ceria reduction? Can the use of controlled synthesis with selectively controlled crystallites surfaces terminations be used as a general tool for studying such structural dependence? Can the results explain the seemingly contradictory comparison between model and high surface area CeO_2 samples?

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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.**

We intend to address the structure dependence of the interaction of CO with cerium oxide. The approach is to first synthesize nano-particulate cerium oxide by different routes, each of which is targeted to selectively produce particles with one particular crystalline termination. The resulting powders will be examined by STEM and by XRD to assess the success of the synthesis routes. The stability and thermal evolution of these nanoparticles will be examined by temperature dependent XRD and by STEM before and after treatment. Then the chemisorptive properties and the activity for CO oxidation for each material will be examined. Comparison of the results for the different crystallites should lead to an improved understanding of the structural dependence of the CO interaction with ceria and of the redox reaction.

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 have prepared and examined model $CeO_2(111)$ surfaces using oriented films in UHV system, but we intend to use CNMS facilities to prepare and study morophologically controlled nanomaterials. We will provide extensive on-site presence to help accomplish each of the research Tasks.

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)

Task 1: *Synthesis of oriented CeO_2 nanoparticles*. Previous results have demonstrated that {1 0 0} terminated nanocubes of CeO_2 can be prepared using a solvothermal method [6]. This synthesis utilizes Ce nitrate precursor in toluene/water, where the nitrate precursor is hydrolyzed and oxidized to CeO_2 with oleic acid to template growth. Hydrothermal conditions with cerium nitrate can also be used to synthesize nanorods with primarily {110} and {100} orientation [7]. Other routine synthesis conditions lead to a preponderance of {111} oriented crystals since these are the most stable surfaces. Preparation of the {100} nanocubes is selected as the primary goal of this task and we will proceed by repeating the published synthesis of Yang *et al.*. Given sufficient time the other two approaches will also be attempted to obtain a suite of three crystal morphologies. For consistency among the three sample types, solvothermal synthesis capabilities at the CNMS will be used to explore optimal approach to highly uniform {111} faceted particles.

Task 2 *Structural characterization:.* The samples from each synthesis will be examined using STEM to assess the morphology of the crystallites following synthesis and following subsequent treatments.
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Task 3 *Structural stability*: Nanoparticles will require calcination to remove surfactants from the nanocubes or to convert the precursor or to remove residual synthesis components. Calcination may lead to changes in crystallinity and morphology of the nanoparticles. The effects of this processing will be examined by STEM and by XRD. Temperature programmed XRD will be used to monitor the growth of crystallites continuously during calcination.

Task 4 *Chemisorption and reaction studies*: Each of the calcined samples will be examined using pulsed CO chemisorption on the AMI-200 to explore how much CO adsorbs as a function of temperature. Given that sufficient adsorption occurs, TPD will be used to determine desorption temperature and desorption CO/CO_2 ratio. This information will be used to determine the appropriate temperature for volumetric CO adsorption which will then be carried out on the Quantachrome Autosorb. CO adsorption will be compared with BET measurements to determine the relative coverage of CO at the adsorption temperature. Surface species will then be determined using FTIR in the dynamic reactor to determine types of surface species and relate these to surface orientation and structural adsorption sites.

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.**

Three months (elapsed) for attempting three different synthesis approaches, although actual staff time should be a small fraction of elapsed time. This task is anticipated to be the most challenging part of the proposal. Four days to characterize samples by STEM and T programmed XRD. Five days (elapsed) to measure CO uptake using the Quantchrome Autosorb (set up time less). Five days intensive activity for FTIR studies.

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

In our group, we have prepared and examined model $CeO_2(111)$ surfaces under UHV conditions and probed the surface chemistry of pure and Rh-loaded surfaces. We have also examined reducibility of CeO_2 and mixed oxides based upon CeO_2 using XANES. Prof. Smart has several publications and a book chapter, on the subject of the surface chemistry of CeO_2. Dr. Fellow has experience using tailored synthesis of nanomaterials as another means to probe the surface chemistry of ceria and understand ceria based catalysts.

7)

LIST OF REFERENCES - if any (not included in the 2 page limit)

(1) Mullins, D. R.; Overbury, S. H. Journal of Catalysis 1999, 188, 340.
(2) Mullins, D. R.; Zhang, K. Z. Surface Science 2002, 513, 163.
(3) Bunluesin, T.; Gorte, R. J.; Graham, G. W. Applied Catalysis B-Environmental 1998, 15, 107.
(4) Li, C.; Sakata, Y.; Arai, T.; Domen, K.; Maruya, K.-i.; Onishi, T. J. Chem. Soc. Faraday Trans. I 1989, 85, 929.
(5) Nolan, M.; Watson, G. W. Journal of Physical Chemistry B 2006, 110, 16600.
(6) Yang, S.; Gao, L. Journal of the American Chemical Society 2006, 128, 9330.
(7) Zhou, K.; Wang, X.; Sun, X.; Peng, Q.; Li, Y. Journal of Catalysis 2005, 229, 206.

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)