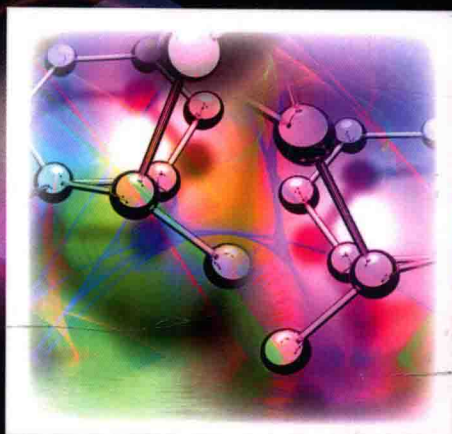


Linda P. Daniels
Editor

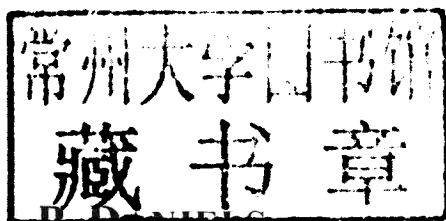
Nanoenergenetics, Nanoparticles and Nanosensors



Nanotechnology Science and Technology

NANOTECHNOLOGY SCIENCE AND TECHNOLOGY

NANOENERGENETICS, NANOPARTICLES AND NANOSENSORS



LINDA P. DANIELS

EDITOR



Nova Science Publishers, Inc.

New York

Copyright © 2011 by Nova Science Publishers, Inc.

All rights reserved. No part of this book may be reproduced, stored in a retrieval system or transmitted in any form or by any means: electronic, electrostatic, magnetic, tape, mechanical photocopying, recording or otherwise without the written permission of the Publisher.

For permission to use material from this book please contact us:

Telephone 631-231-7269; Fax 631-231-8175

Web Site: <http://www.novapublishers.com>

NOTICE TO THE READER

The Publisher has taken reasonable care in the preparation of this book, but makes no expressed or implied warranty of any kind and assumes no responsibility for any errors or omissions. No liability is assumed for incidental or consequential damages in connection with or arising out of information contained in this book. The Publisher shall not be liable for any special, consequential, or exemplary damages resulting, in whole or in part, from the readers' use of, or reliance upon, this material. Any parts of this book based on government reports are so indicated and copyright is claimed for those parts to the extent applicable to compilations of such works.

Independent verification should be sought for any data, advice or recommendations contained in this book. In addition, no responsibility is assumed by the publisher for any injury and/or damage to persons or property arising from any methods, products, instructions, ideas or otherwise contained in this publication.

This publication is designed to provide accurate and authoritative information with regard to the subject matter covered herein. It is sold with the clear understanding that the Publisher is not engaged in rendering legal or any other professional services. If legal or any other expert assistance is required, the services of a competent person should be sought. FROM A DECLARATION OF PARTICIPANTS JOINTLY ADOPTED BY A COMMITTEE OF THE AMERICAN BAR ASSOCIATION AND A COMMITTEE OF PUBLISHERS.

Additional color graphics may be available in the e-book version of this book.

LIBRARY OF CONGRESS CATALOGING-IN-PUBLICATION DATA

Nanoenergenetics, nanoparticles, and nanosensors / editor, Linda P. Daniels.

p. cm.

Includes index.

ISBN 978-1-61761-764-5 (hardcover)

1. Nanostructured materials. I. Daniels, Linda P.

TA418.9.N35N249 2010

620'.5--dc22

2010033081

Published by Nova Science Publishers, Inc. † New York

NANOTECHNOLOGY SCIENCE AND TECHNOLOGY

**NANOENERGENETICS,
NANOPARTICLES AND
NANOSENSORS**

NANOTECHNOLOGY SCIENCE AND TECHNOLOGY

Additional books in this series can be found on Nova's website
under the Series tab.

Additional E-books in this series can be found on Nova's website
under the E-books tab.

PREFACE

Nanotechnology is a “catch-all” description of activities at the level of atoms and molecules that have applications in the real world. A nanometer is a billionth of a meter, about 1/80,000 of the diameter of a human hair, or 10 times the diameter of a hydrogen atom. Nanotechnology is now used in precision engineering, new materials development as well as in electronics; electromechanical systems as well as mainstream biomedical applications in areas such as gene therapy, drug delivery and novel drug discovery techniques. This book presents the latest research in this field.

Chapter 1- For the past several years, our group has been exploring materials in which energy can be trapped in metastable states, in an attempt to understand a phenomenon termed Structural Bond Energy Release (SBER). The SBER concept originated with experiments conducted in the U.S. in the 1930s by Bridgman (1), in which various inert common materials, such as chalk and sugar, were compressed in a Bridgman anvil cell and subjected to shear. For several materials, the combination of pressure and shear resulted in a rapid liberation of energy. These experiments generated intense interest in the former Soviet Union (FSU) (2, 3), yet were virtually ignored by the rest of global scientific community. Since researchers in the FSU had a particular interest in carbon, we performed theoretical calculations to characterize high-pressure states (> 600 GPa) of this potential SBER material. We initially began searching for features in the phase diagrams of carbon that would suggest sharp thresholds for shock-induced polymorphic phase transition; our calculations began with the shock Hugoniot of diamond to investigate the existence of possible anomalies that could result in the identification of new, high-pressure metastable phases of carbon. However, no such anomalies were identified.

Chapter 2- All photoelectric devices capture solar energy by the generation of a higher-energy mobile electron upon illumination by the sun. The mobile electron can be harnessed to create electricity; however, in a semiconductor-based solar cell, the mobile electron leaves behind a positive hole within the material that can recombine with the electron, thus reducing efficiency. For the case of a semiconductor photocell, an electric field is used to reduce this recombination.¹ These carriers are then transported to electrodes where they become the basis of an electrical current. Current state-of-the-art high-efficiency cells use a combination of semiconductors with different band gaps to capture a larger portion of the solar spectrum. Although the efficiency of some of these advanced photovoltaic cells is high with conversion efficiencies nearing 50%, the main drawback of these technologies is the high cost. In addition, semiconductor-based solar cells do not work well under low-light conditions where they suffer a “cutout” at some lower limit of illumination, when charge carrier mobility is low and recombination becomes a major issue. However, there is another method to separate the electron and holes that mimic the method of photosynthesis. These cells are called dye-sensitized solar cells or DSSCs.² As a result of low losses and a lack of recombination unlike semiconductor-based systems, DSSCs work even in low-light, cloudy sky conditions. In addition, they are fabricated using inexpensive processing methods and materials. Furthermore, the cells can be made flexible. These features will be critical to the warfighter needing to fight under all weather conditions.

Chapter 3- The feasibility of a novel approach for studying the chemical reactions between metallic nanoparticles and molecular explosives has been demonstrated. This method is based on the production of nanoparticles in a laser-induced plasma and the simultaneous observation of the time-resolved atomic and molecular emission characteristic of the species involved in the intermediate chemical reactions of the nanoenergetic material in the plasma.

Chapter 4- The development and tailoring of new energetic materials is critical to the success of explosives, propellants, micro-actuation, and power for next generation DoD weapons and microsystems. Specifically, engineering silicon (Si) for nanoenergetics provides a means to readily integrate energetic material with microsystems. Since the oxidation of Si is much more exothermic than most carbon based materials, it can be engineered to be highly explosive. Furthermore, nanostructured materials can store higher amounts of energy than conventional energetic materials and deliver faster energy release due to their increased surface area.

The nanoenergetic field is relatively young, but already several material systems and processes are being explored [1]. However, since Si is inexpensive, well characterized, and the cornerstone of the microelectromechanical systems (MEMS) industry, it will play an important role in this field. If Si can be tailored for the nanoenergetics field, a host of applications will soon follow.

Chapter 5- Nanoparticles have interesting physical properties that often vary from the bulk material. Some of these properties, including increased reactivity [1], are due to the high surface area to volume ratio of nanoparticles. With that in mind, nanoparticles may provide enhanced energy release rates for explosive and propellant reactions [2].

There is considerable interest in the self-propagating high-temperature synthesis (SHS) reactions of intermetallic compounds because of the associated energy release that takes place [3] during the alloying reaction. In addition to the energetic reaction observed in these materials, it is possible to produce structural materials that contain this energy release property. Once ignited, the SHS reaction releases a large amount of energy in a short period of time. One significant difference between SHS and typical combustion processes is that the reactants and products are confined to the condensed state [4]. The SHS process has many potential applications where heat generation is required and oxygen is not available or gaseous products are not desirable. These include alloy formation, net-shape processing, propellants, and use as initiators. One of the compounds formed from the SHS reaction, and studied here, is nickel aluminide (NiAl). NiAl is an important alloy because of its desirable high temperature strength and oxidation resistance [5] and the high energy of formation [6]. Recently Weihs and coworkers have also used NiAl nanolaminate systems in applications of reactive welding [7].

Chapter 6- Nanoparticles are often used in applications where a high surface-area-to-volume ratio is desired. Some typical applications include catalysis, biosensors, and use as drug delivery vehicles [1, 2]. A major limitation of the expanded use of these nanoparticles is that the fabrication of nanoparticles with the desired morphology and structure is challenging [3–5]. Gold is a commonly used material because of its resistance to oxidation and its interesting electrical, magnetic, optical, and physical properties [6]. Furthermore, there is a considerable knowledge base on functionalizing gold surfaces that are being ported to analogous particles [7]. For this reason, gold nanoparticles are commonly chosen for basic research because of the availability of experimental [8, 9] and atomistic simulation data [10, 11]. For instance, using x-ray powder diffraction, Cleveland et al. [9] discovered that

small 10- to 20-Å-diameter gold nanoparticles form a truncated-decahedral motif geometry. Using molecular dynamics (MD) simulations, Lewis et al. [12] were able to determine the melting process for gold nanoparticles. This last result is important because the authors found that the surface atoms melt first and at a temperature below that of the atoms in the core of the nanoparticle. The implications of this for coated nanoparticles are that the surface atoms, where binding of the monolayer takes place, are affected by a lower temperature than is expected from the melting temperature of the whole nanoparticle. The results of these past efforts are built upon in this work in order to analyze in larger gold nanoparticles the nature and role of surface functionalization.

Chapter 7- The Army does not have a sensing technology that meets both the chemical selectivity and sensitivity requirements for detection of a wide range of explosive compounds. Our approach aims to address this significant shortfall through the combination of two separate technologies, MIPs and SERS. Although each technology has been separately studied in the literature with limited success, this report is the first successful integration and demonstration of this multifunctional approach for explosives detection to date. In this first-year effort, we have clearly validated the MIP-SERS concept to include the development of an integration strategy and MIP formulation that has excellent adhesion properties, along with a demonstration of integrated SERS detection. Although not planned in the first-year objectives, we have demonstrated a greater selectivity of the imprinted polymer for 2,4,6-trinitrotoluene (TNT) over other nitro- containing compounds. Initially, we chose a commercially available SERS substrate platform to validate the sensing concept; however, we aim to address the required sensitivity through more advanced substrate development and integration approaches as the project continues.

Chapter 8- There is a critical need to develop enhanced soldier protection against chemical and biological warfare agents in full spectrum operation and soldier protection in counter-insurgency environment. There is a need to detect, identify, and neutralize chemical, biological, radiological or nuclear (CBRN) threats as identified in the Future Force (FF) and Current Force (CF) Capability Gaps (FF1, FF3, FF6, CF4, CF7).

There is also a critical need to detect explosive hazards such as improvised explosive devices (IEDs) and mines before they can affect the soldier or system's ability to maintain momentum of the maneuver forces and the ability to detect IEDs and mines from safe stand-off distance (FF1, FF3, FF6, CF4, CF5, CF6, CF7). Current systems to address these needs are too bulky, take longer (several minutes) detection times, and often unsuitable for dismounted soldier application.

CONTENTS

Preface		vii
Chapter 1	Exploiting Unique Features of Nanodiamonds as an Advanced Energy Source <i>William D. Mattson, Radhakrishnan Balu, Betsy M. Rice and Jennifer A. Ciezak</i>	1
Chapter 2	Biomimetic Approach to Solar Cells Based on TiO ₂ Nanotubes <i>Jan L. Allen, Ivan C. Lee and Jeff Wolfenstine</i>	11
Chapter 3	Investigation of Chemical Processes Involving Laser-Generated Nanoenergetic Materials <i>Jennifer L. Gottfried</i>	21
Chapter 4	Characterization and Improvements to Porous Silicon Processing for Nanoenergetics <i>Collin Becker, Luke Currano and Wayne Churaman</i>	33
Chapter 5	Molecular Dynamics Simulation of the Kinetic Reaction of Nickel and Aluminum Nanoparticles <i>Brian J. Henz, Takumi Hawa and Michael Zachariah</i>	47
Chapter 6	Mechano-Chemical Stability of Gold Nanoparticles Coated with Alkanethiolate SAMs <i>Brian J. Henz, Takumi Hawa and Michael R. Zachariah</i>	77

Chapter 7	A Nanosensor for Explosives Detection Based on Molecularly Imprinted Polymers (MIPs) and Surfaced-Enhanced Raman Scattering (SERS) <i>Ellen Holtoff and Dimitra Stratis-Cullum</i>	111
Chapter 8	Real-Time Intelligent Chemical and Biological Nanosensors on Flexible Platform <i>Govind Mallick, Shashi P. Karna and Pulickel M. Ajayan</i>	129
Chapter Sources		139
Index		141

Chapter 1

EXPLOITING UNIQUE FEATURES OF NANODIAMONDS AS AN ADVANCED ENERGY SOURCE

***William D. Mattson, Radhakrishnan Balu, Betsy M. Rice
and Jennifer A. Ciezak***

1. OBJECTIVE

For the past several years, our group has been exploring materials in which energy can be trapped in metastable states, in an attempt to understand a phenomenon termed Structural Bond Energy Release (SBER). The SBER concept originated with experiments conducted in the U.S. in the 1930s by Bridgman (1), in which various inert common materials, such as chalk and sugar, were compressed in a Bridgman anvil cell and subjected to shear. For several materials, the combination of pressure and shear resulted in a rapid liberation of energy. These experiments generated intense interest in the former Soviet Union (FSU) (2, 3), yet were virtually ignored by the rest of global scientific community. Since researchers in the FSU had a particular interest in carbon, we performed theoretical calculations to characterize high-pressure states (> 600 GPa) of this potential SBER material. We initially began searching for features in the phase diagrams of carbon that would suggest sharp thresholds for shock-induced polymorphic phase transition; our

calculations began with the shock Hugoniot of diamond to investigate the existence of possible anomalies that could result in the identification of new, high-pressure metastable phases of carbon. However, no such anomalies were identified.

During the course of the earlier theoretical investigation, however, we became aware of a combined experimental/theoretical study on surface reconstructions in nanodiamonds (NDs) (4) that suggest such crystallites might contain significant SBE. The theoretical portion of this study used semi-empirical tight binding to predict the equilibrium structure of ND; the results indicated that surface reconstruction of ND of various sizes from 1.2 to 3.0 nm occurred, in which the surface atoms repositioned themselves into fullerene-type geometrical arrangements spontaneously at low temperatures. Both the experimental and theoretical results support the existence of these “bucky diamonds, i.e., carbon nanoparticles with a diamond core of a few nanometers and a fullerene-like surface structure” (4). The calculations revealed tensile stress on the core of the nanocluster, implying that the reconfiguration of the fullerene-like surface compresses the diamond core. Our own calculations of the diamond shock Hugoniot (5) indicate that very small degrees of compression produce huge increases in pressure. Thus, any subtle changes in the bonding structure of the outer shell that produce minor bond length modifications within the ND core could generate significant stored structural bond energy within the ND. In addition to the structural strain within the core, the interfacial strain between the fullerene-type shell and the diamond core may contribute to the total stored structural energy. These findings suggest the SBER potential of bucky diamonds, in that a sudden disruption of the shell and subsequent relaxation of the internal pressure of the core might result in the destruction of the diamond structure with an accompanying energy release. To explore this possibility, a joint experimental/quantum mechanical study investigated the feasibility of SBER phenomenon in ND.

2. APPROACH

2.1. Experimental

Piston-cylinder type diamond anvil cells with 300 μm diamond culets were used for all static high-pressure experiments. Raw (NB-90) and Oxidized (NB90-OX) nanodiamond suspensions, were obtained from NanoBlox, Inc.

The suspensions were dried in a drying oven at 150 °C over the course of several days and then ground into a fine powder. A 60–100 μm ND sample was loaded into the sample well (~ 120 μm in diameter) of a rhenium gasket. The pressure within the diamond anvil cell was determined from the frequency shift of the ruby R_1 fluorescence line (6). Raman spectra were obtained from an Ar^+ ion laser operating at 514.5 nm with an optical system previously described (7), and a laser spot diameter of ~ 4 μm at room temperature. Prior to any experimental measurements, a wavelength calibration of the spectrograph was performed with a Neon lamp; this method of calibration has an accuracy of ± 1 cm^{-1} . The spectral resolution for all Raman measurements was ± 4 cm^{-1} .

2.2. Theoretical

For all calculations, the PBE form of the Generalized Gradient Approximation (GGA) of the Density Functional Theory (DFT) as implemented in the local orbital basis code CP2K was used. We employed a Gaussian basis and an auxiliary plane wave basis with the kinetic energy cutoff of 400 Rydberg. All the calculations were performed at the Γ points of the Brillouin zone, as the unit cells were quite large. The SCF convergence tolerance at each step of the Quantum Molecular Dynamics (QMD) calculations for all systems studied was 1×10^{-5} a.u. Each ND was composed of 2052 atoms, and an initial optimized geometry was obtained by cleaving a sphere out of the bulk diamond with a diameter of 2.6 nm. The ND was allowed to relax in QMD simulations in the microcanonical (NVT) ensemble ($T=300$ K) in a simulation cell with edge length of 121.5 bohr. The reference system propagator algorithms (RESPA) implementation of the NVT ensemble implemented in CP2K was employed for the simulations of the collisions. Trajectories of the collisions were performed using a step size of 1 fs. In order to simulate a hypervelocity collision, atomic velocities for the colliding ND were assigned velocities above thermal to correspond to 10 km/s, allowing for a 20 km/s relative collision velocity. Only off-center collisions were explored.

3. RESULTS

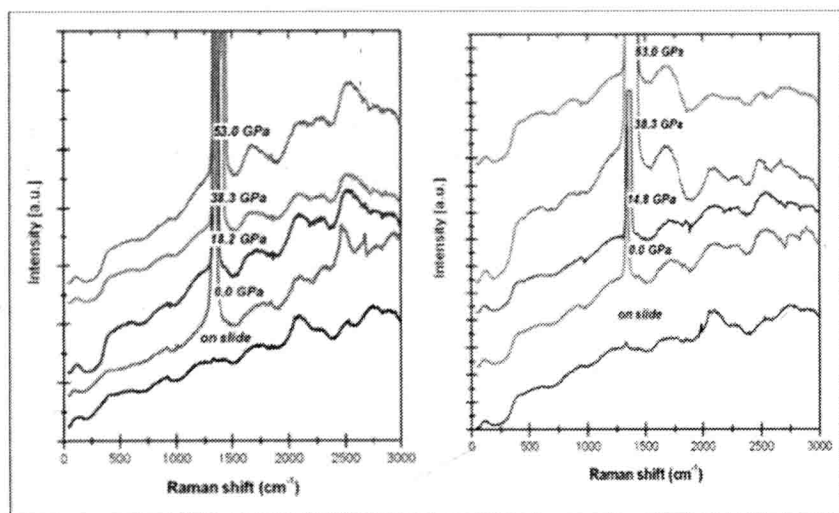
3.1. Experimental

The Raman spectra of the Raw (RND) and Oxidized (OND) on isothermal compression ambient to 53 GPa are shown in Figure 1 (left and right frames, respectively). Although there are similarities between the Raman spectra of the bulk single crystal (SC) diamond and micro/nanodiamond, the finite particle size of the ND results in obvious spectroscopic differences, such as shifts in the vibrational frequencies and a generalized broadening of the bands (8, 9). These differences are readily apparent in figure 1 where the sharp feature near 1330 cm^{-1} arises from the first order scattering from the diamond (single crystal) anvils, and the remaining weak, broad features arise from the nanodiamonds. The Raman spectra of both ND samples show the appearance of a broad shoulder ($\sim 1260\text{ cm}^{-1}$) on the low frequency side of the 1335 cm^{-1} SC feature near 15 GPa. Previous studies have shown that the vibrational position of this shoulder lies within the spectral range associated with the partial density of states of the diamond lattice, and indicates that the ND particles have a composite structure consisting of a diamond core and an amorphous carbon shell (10). At pressures near 15 GPa, the feature appears more intense in the RND, but with increasing pressure, the intensity in the corresponding OND spectra increases nearly two fold. The increase in the intensity of the OND feature is consistent with a thinner amorphous carbon surface structure, which would then expose the diamond core as pressure increases. An increase in the amount of exposed core is expected to be a precursor to an SBER event.

In addition to the sp^3 diamond feature, two very broad bands near 1000 cm^{-1} , and between 1500 cm^{-1} and 1800 cm^{-1} , are observed in the Raman spectra of both samples. The broad band between 1500 cm^{-1} and 1800 cm^{-1} can be interpreted as a superposition of two peaks at 1630 cm^{-1} and 1750 cm^{-1} . The band near 1630 cm^{-1} is associated with sp^2 hybridized graphite, while the 1750 cm^{-1} is thought to originate from C=O functionality on the ND surface (10). These features are often observed in vibrational spectra of amorphous carbon samples that contain a high concentration of carbon atoms in mixed sp^2/sp^3 hybridization states (11–13). Since the most probable end product of a ND SBER type phase transition is graphite, a transition would be indicated in the Raman vibrational spectrum by a sharp increase in the sp^2 peak centered near 1630 cm^{-1} . The intensity of this feature in the RND spectrum remains

fairly consistent over the pressure range studied, indicating that little to no transition occurs. This may be the result of thick amorphous carbon surface, as well as the sample impurities. However, in the OND spectra, there is a nearly two-fold intensity increase in the sp^2 feature that correlates well with the intensity increase of the 1260 cm^{-1} feature. This suggests that a partial phase transition from sp^3 hybridized diamond to sp^2 hybridized graphite may be occurring, but it is sluggish.

3.2. Theoretical



Note: Spectra are offset for viewing ease.

Figure 1. Raman spectra of raw (left) and oxidized (right) nanodiamonds as a function of pressure.

DFT calculations were used to characterize a bare, reconstructed ND composed of 2052 atoms; the optimized structure of this ND is shown in figure 2. The bonds within the core were analyzed by calculating the average distance from an atom to its four nearest neighbors. These averages were then binned and averaged by the distance of the atom from the center of the nanodiamond. These bond lengths were then compared to the bond lengths of bulk diamond to provide estimates of the internal pressure of the core by comparing local bond structure to that of bulk diamond at known pressure. Although the material near the surface is significantly distorted from that of