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Boron Nitride-Based Aerogels With Tunable Properties

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REGENTS OF THE UNIVERSITY OF CALIFORNIA

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Final Report

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14. ABSTRACT
Investigation of aerogels containing boron and nitrogen. Synthesis methods are partial or complete conversion from graphene aerogels, and surface coating of aerogels followed by heat treatments. Characterization includes TEM, SEM, Raman, FTIR, NMR, and XPS. Theoretical modeling of B and N containing carbon lattices to determine most favorable local atomic configurations. Applications include chemical sensors based on BxCyNz aerogel frameworks, with and without additional coatings.

15. SUBJECT TERMS
Aerogels, boron nitride, boron and nitrogen doping, graphene, chemical sensors

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BN-Based Aerogels with Tunable Properties
AFOSR Grant FA9550-14-1-0323

Reporting Period (since last report submission): 9/15/17 to 9/14/18
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Alex Zettl (PI, U.C. Berkeley), Marvin L. Cohen (co-PI, U.C. Berkeley), Marcus Worsley (co-PI, Lawrence Livermore National Laboratory)

Accomplishments

During the last period of performance the team investigated $B_xC_yN_z$ aerogels via the incorporation of boron and topological defects into graphene aerogels, and constructed and characterized hybrid WS_2/graphene aerogels.

Boron-doped and defect-engineered graphene aerogels were prepared using triphenyl boron as a boron precursor followed by selected heat treatments. The boron chemistry and concentration in the graphene lattice were found to be highly dependent on the temperature used to activate boron. At 1500 °C, boron was incorporated at 3.2 atom % through a combination of B−C, B−N, and B−O bonds. At 1750 °C, the boron concentration decreased to 0.7 atom % and was predominantly incorporated through B−N bonding. Higher temperatures resulted in complete expulsion of boron from the lattice, leaving behind defects that were found to be beneficial for NO_2 gas detection. The gas sensing properties were explored to gain insight into the impact of boron chemistry on the sensing performance. A highly sensitive and selective conductometric NO_2 sensor was fabricated on a low-power microheater. Defect-engineered graphene aerogels with no boron remaining were found to have superior gas detection properties for NO_2. At an optimum sensing temperature of 240 °C, the defect-engineered aerogel displayed a detection limit of 7 ppb for NO_2 and response and recovery times of 100 and 300 s, respectively, with excellent selectivity over ammonia and hydrogen. The superior gas sensing performance of defect-engineered graphene aerogels has remarkable implications for their performance in catalysis and energy storage applications.

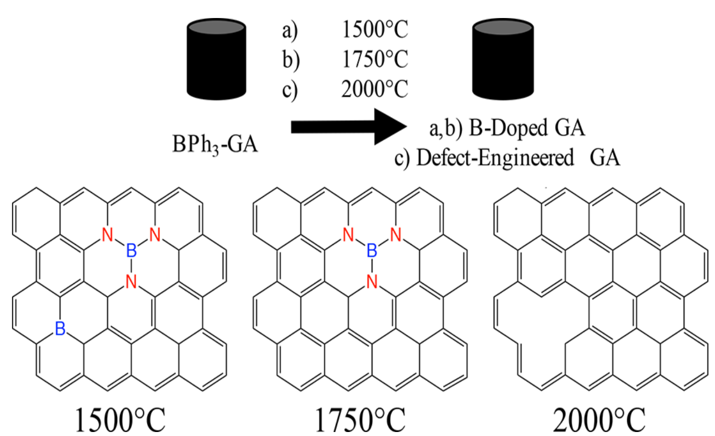

Fig. 1. Process of creating B-doped and defect-engineered BxCyNz aerogels. Heat treatments at one of the three indicated temperatures leads to different atomic configurations in the crystalline lattice.

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WS_2/graphene aerogel (WS_2/GA) composite aerogels were fabricated and characterized structurally and for gas sensing applications. In order to probe the gas sensing performances of the WS_2/GA, a sensor was fabricated by integrating WS_2/GA with a microfabricated two-electrode device. The WS_2/GA was characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman spectroscopy, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and nitrogen porosimetry.

This system was also tested for NO_2 gas detection capability. NO_2 is an increasing problem for air quality worldwide. The gas can cause serious problems such as lung damage, acid smog or rain. As little as 50 ppb can cause airway inflammation in lungs. Additionally, humidity is not a well-characterized parameter in practical environments. The detection of NO_2 at ppb-level concentrations in harsh environment (such as high humidity and high temperature) requires advances in sensing materials to provide the necessary performance characteristics. In previous reports, most NO_2 sensors working under high humidity were based on metal oxides and yttria-stabilized zirconia (YSZ). For these sensors, the detection concentration of NO_2 is high (>1 ppm) or the sensitivity to NO_2 decreased rapidly with time. This hybrid nanomaterial was found to improve the selectivity to NO_2, compared to control graphene and WS_2 aerogels.

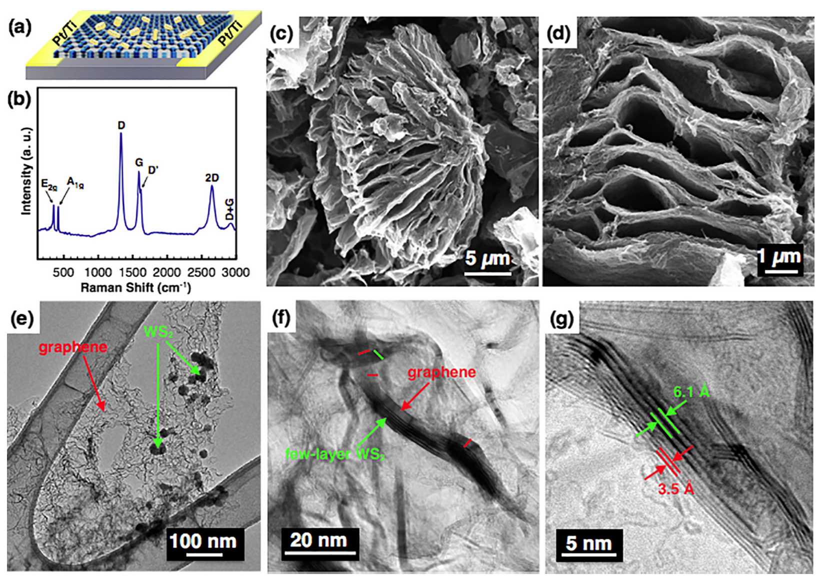

Fig. 2. (a) Schematic diagram of the resistive WS2/GA-based sensor. (b) Raman spectrum of WS_2/GA. (c, d) SEM images of WS_2/GA on sensor device. TEM images of the as-prepared WS_2/GA: (e) low magnification image, (f, g) high resolution images, showing the graphene is coated by few-layer WS_2.

The NO_2 sensing performance of the WS_2/GA-based sensors was investigated under different relative humidities (0–60%), and ambient temperatures (room temperature (RT) to 180 ^oC). In all cases, the sensors exhibited p-type behavior. In dry atmosphere, faster response and better recovery were obtained with increasing temperature, reaching optimum sensing performance around 180 ^oC. At room temperature, interestingly, humidity was found helpful for enhancing the response and recovery of the sensor to NO_2. Detection limits in the range of 10–15 ppb NO_2 were determined. A possible gas sensing mechanism for this composite aerogel was proposed.

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Publications during reporting period:

Peer-Reviewed Papers

1) Sally Turner, Wenjun Yan, Hu Long, Art J. Nelson, Alex Baker, Jonathan R. I. Lee, Carlo Carraro, Marcus A. Worsley, Roya Maboudian, and Alex Zettl. Boron Doping and Defect Engineering of Graphene Aerogels for Ultrasensitive NO2 Detection. J. Phys. Chem. C 2018, **122** 20358-20365 DOI: 10.1021/acs.jpcc.8b05984

2) Wenjun Yan, Marus A. Worsley, Thang Pham, Alex Zettl, Carlo Carraro, Roya Maboudian. Effects of ambient humidity and temperature on the NO2 sensing characteristics of WS2/graphene aerogel. Applied Surface Science 2018, **450** pp. 372-379 https://doi.org/10.1016/j.apsusc.2018.04.185

3) D. Kraus, N.J. Hartley, S. Frydrych, A.K. Schuster, K. Rohatsch, M. Rodel, T.E. Cowan, S. Brown, E. Cunningham, T. van Driel, L. B. Fletcher, E. Galtier, E. J. Gamboa, A. Laso Garcia, D. O. Gericke, E. Grenados, P.A. Heimann, H. J. Lee, M. J. MacDonald, A. J. Mackinnon, E. E. McBride, I. Nam, P. Neumayer, A. Pak, A. Pelka, I. Prencipe, A. Ravasio, R. Redmer, A. M. Saunders, M. Scholmerich, M. Schorner, P. Sun, S. J. Turner, A. Zettl, R. W. Falcone, S. H. Glenzer, T. Toppner, and J. Vorberger. High-pressure chemistry of hydrocarbons relevant to planetary interiors and intertial confinement fusion. Physics of Plasmas **25**, 056313 (2018); doi: 10.1063/1.5017908

Conference Talks

Sally Demaio-Turner
“Introduction of New Boron Chemistries into Graphene Aerogels—Synthesis and Properties”
Materials Research Society Fall Meeting 2017 (Nov 26 – Dec 1)

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