Computational Chemistry Research on NETL Supercomputing System

General Capabilities of the Atomistic Scale Research

NETL Supercomputer capabilities represent an immense progress and support for development of atomistic scale computational research performed at NETL. These facilities allowed the use of state of the art computational techniques to predict with high accuracy the chemical and physical processes that govern the end-use properties of energy technologies, to accelerate the discovery of new materials and chemical processes and to enhance the performances of the current energy technologies. A diverse ensemble of computational approaches were facilitated by the use of the Supercomputer systems including first principles quantum mechanics calculations for gas phase and periodic systems, classical and quantum molecular dynamics simulations in various statistical ensembles, Monte Carlo simulations and microkinetic modeling. The computational models developed were use also to guide the experimental development of novel materials with optimized properties.

The availability of NETL Supercomputer system has facilitated research projects with direct impact on various technologies ranging from catalyst development for syngas and natural gas conversion, catalytic systems for CO_2 utilization processes, development of optimized solid sorbents for CO_2 capture, identification of novel ionic liquid and hybrid nanostructured membranes for CO_2 gas separation, as well as novel nanostructured composite materials for energy conversion and new gas sensor materials. The supercomputing capabilities at NETL allowed the analysis of large atomic, molecular and crystalline systems, use of highly accurate but computational very demanding first principles calculations with periodic boundary conditions, screening of a large number of crystalline structures as in the case of solid sorbent developments, or testing of a large number of binding configurations in complex nanoporous materials.

The importance of the work perform is also reflected by the large number of publications obtained in this area. Practically all members of the computational group have obtained several important publications in 2013-2014 period using NETL Supercomputer capabilities. Here is just a short personal list:

1) D. C. Sorescu, S. Civiš, and K. D. Jordan "**Mechanism of Oxygen Exchange between CO_2 and TiO_2(101)**", J. Phys. Chem. C. 2014, 118, 1628 (dx.doi.org/10.1021/jp410420e).

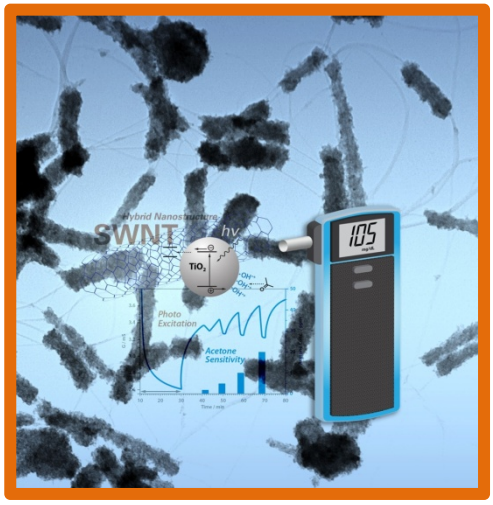
2) Y. Duan, H. Pfeiffer, B. Li, I. C. Romero-Ibarra, D. C. Sorescu, D. R. Luebke, and J. W. Halley "**CO_2 Capture Properties of Lithium Silicates with Different Ratios of Li_2O/SiO_2: An Ab initio Thermodynamic and Experimental Approach**", Phys.Chem.Chem.Phys.,2013, 15, 13538-13558 (doi: 10.1039/c3cp51659h)

3) M. Ding, D. C. Sorescu, A. Star "**Photoinduced Charged Transfer and Acetone Sensitivity of Single-Wall Carbon Nanotube-Titanium Dioxide Hybrids"** J. Am. Chem. Soc. 2013, 135, 9015-9022 (doi: 10.1021/ja402887v).

4) J. Lee, D. C. Sorescu, X. Deng, and K. D. Jordan "**Water Chain Formation on TiO_2(110)**", J. Phys. Chem. Lett. 2013, 4, 53-57 (doi:10.1021/jz301727n).

Specific examples of success stories are numerous. These have received direct attention of scientific community as reflected by journal publications and the associated large number of comments on various scientific blogs.

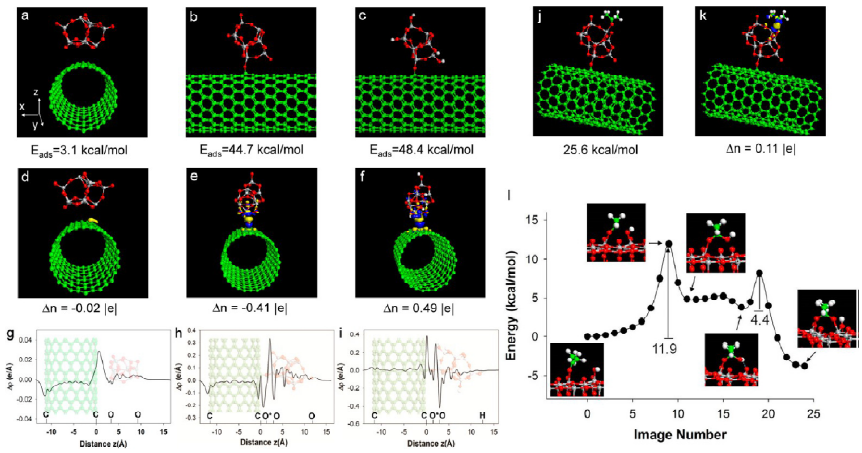
Sensors Area:New Breathalyzer Offers the Potential for Non-invasive Diabetes Monitoring



A recent R&D innovation from the National Energy Technology Laboratory and its Regional University Alliance (NETL-RUA) has the potential to simplify diagnosis of diabetes through acetone detection. The NETL-RUA has developed a new hybrid nanostructure material that may be used in an inexpensive "breathalyzer" to test for and monitor diabetes.

NETL-RUA researchers discovered that by bolstering titanium dioxide—the same ingredient found in most sunscreens—with carbon nanotubes, or CNTs, they could produce a sensor that can detect acetone vapors at parts per million levels. Carbon nanotube (CNT)-based sensors are extremely small, inexpensive, consume little to no power, and are compatible with complementary metal-oxide-semiconductor (CMOS) technology, which allows further incorporation into modern electronic devices, like smart phones. These advantages make CNT-based sensors ideal for chemical sensing and non-invasive medical diagnostic tools.

NETL supercomputing capabilities were essential in order to explain the binding, reactivity and the charge transfer that take place upon adsorption of acetone on the nanohybrid titanium dioxide-carbon nanotube system.



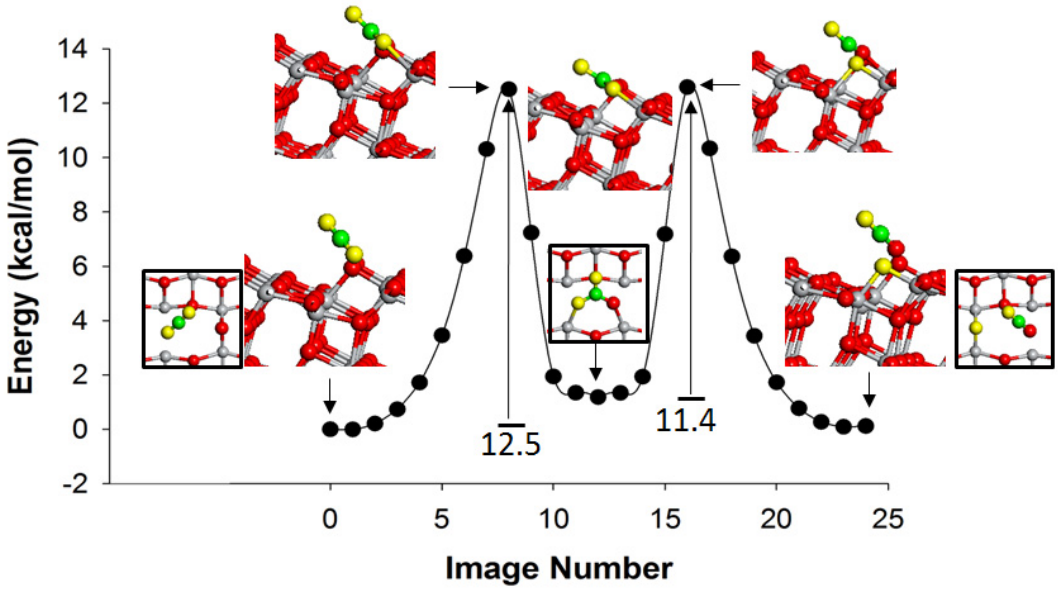
The results of this combined experimental and theoretical study were recently published in the premier *Journal of the American Chemical Society*:Photoinduced Charge Transfer and Acetone Sensitivity of Single-Walled Carbone Nanotube –Titanium Dioxide Hybrids by M.Ding, D.C. Sorescu, A.StarJ. Am. Chem.Soc. 2013, 135, 9015.

Catalysis Area: Investigation of the reactivity mechanism of CO_2 interacting with Anatase Surface

Conversion of CO_2 to marketable products represents an important research area in the overall ensemble of strategies considered to alleviate the environmental impact of greenhouse emissions. In this regard, TiO_2 has been identified as a promising candidate material capable to initiate CO_2photoreduction. The efficiency and selectivity of this process require however further optimization in order to provide viable solutions for CO_2 conversion to useful chemicals. A prerequisite for further scientific progress in this area isenhanced understanding of the interactions between CO_2 andTiO_2 surfaces.

Such problems have been addressed by using first principles calculations performed on NETL Supercomputer systems. Computational research performed in this case has been able to identify the reaction mechanism and to identify the chemical intermediates formed during activation of CO_2 and its reactions with oxide surface. In a recent study the mechanism of oxygen exchange between CO_2 and a defective anatase(101) surface was investigated based on density functional theory calculations with inclusion of long-range dispersion interactions and

on-site Coulomb interactions. This study identifies the key intermediate species responsible for the oxygen exchange mechanism consistent to experimental observed phenomena..



The results of this theoretical study were recently published in The Journal of Physical Chemistry C: “Mechanism of Oxygen Exchange between CO2 and TiO2(101) Anatase”, D. C. Sorescu, S. Civis, and K. D. Jordan, J. Chem. Phys. C 2014, 118, 1628.