Announcing the Final Examination of Takat Rawal for the Degree of Doctor of Philosophy in Physics

Date: Friday, April 7, 2017

Time: 10:00 a.m.

Room: PSB 248

Dissertation title: Predictive Modeling of Functional Materials for Catalytic and Sensor Applications

Abstract:

The research conducted in my dissertation focuses on theoretical and computational studies of the electronic and geometric structure, and catalytic and optical properties of functional materials in the form of nano-structures, extended surfaces, two-dimensional systems and hybrid structures. The fundamental aspect of my research is to predict nanomaterial properties through *ab-initio* calculations using methods such as quantum mechanical density functional theory (DFT) and kinetic Monte Carlo simulation, which help rationalize experimental observations, and ultimately lead to the rational design of materials for the electronic and energy-related applications.

Focusing on the popular single-layer MoS_2, I first show how its hybrid structure with 29-atom transition metal nanoparticles (M_{29} where M=Cu, Ag, and Au) can lead to composite catalysts suitable for oxidation reactions. Interestingly, the effect is found to be most pronounced for Au_{29} when MoS_2 is defect-laden (S vacancy). Second, I show that defect-laden MoS_2 can be functionalized either by deposited Au nanoparticles or when supported on Cu(111) to serve as a cost-effective catalyst for methanol synthesis *via* CO hydrogenation reactions. The charge transfer and electronic structural changes in these sub systems lead to the presence of "frontier" states near the Fermi level, making the systems catalytically active.

Next, in the emerging area of single site catalysts, I provide rationale for the viability of single Pd sites stabilized on ZnO($10\bar{1}0$) as the active sites for methanol partial oxidation, an important reaction for the production of H_2. We trace its excellent activity to the modified electronic structure of the single Pd site as well as neighboring Zn cationic sites. With the DFT-calculated activation energy barriers for a large set of reactions, we perform *ab-initio* kMC simulations to determine the selectivity of the products (CO_2 and H_2). These findings offer an opportunity for maximizing the efficiency of precious metal atoms, and optimizing their activity and selectivity (for desired products).

In related work on extended surfaces while trying to explain the Scanning Tunneling Microscopy images observed by our experimental collaborators, I discovered a new mechanism involved in the process of Ag vacancy formation on Ag(110), in the presence of O atoms which leads to the reconstruction and eventually oxidation of the Ag surface. In a similar vein, I was able to propose a mechanism for the orange photoluminescence (PL), observed by our experimental collaborators, of a coupled system of benzylpiperazine (BZP) molecule and iodine on a copper surface. Our results show that the adsorbed BZP and iodine play complimentary roles in producing the PL in the visible range. Upon photo-excitation of the BZP-I/CuI(111) system, excited electrons are transferred into the conduction band (CB) of CuI, and holes are trapped by the adatoms. The relaxation of holes into BZP HOMO is facilitated by its realignment. Relaxed holes subsequently recombine with excited electrons in the CB of the CuI film, thus producing a luminescence peak at ~2.1 eV. These results can be useful for forensic applications in detecting illicit substances.

Outline of Studies:

Major: Physics

Educational Career:

M. S. University of Central Florida, USA, 2012

B. S. Tribhuvan University, Nepal, 2007

Committee in Charge:

Dr. Talat S. Rahman (Chair)

Dr. Zhengu Chang

Dr. Michael N. Leunberger

Dr. Shengli Zou (External Committee Member)

Approved for distribution by Dr. Talat S. Rahman, Committee Chair, on March 30, 2017.