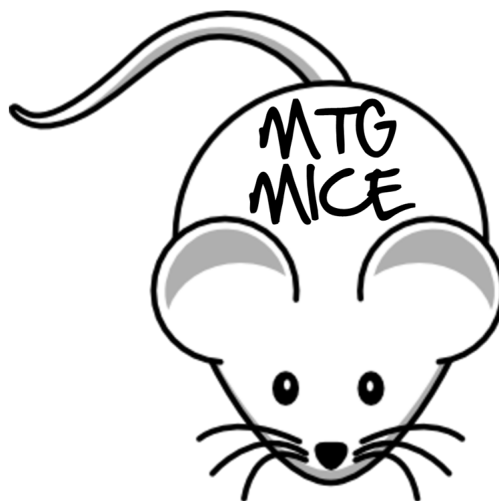
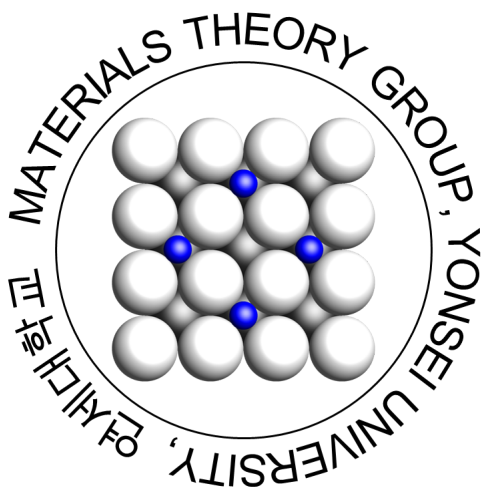


2015 Winter MICE

The 8th Materials Information,  
Characterization, and Exploration  
(MICE-8)

B127, Engineering Building B, Yonsei University,  
Seoul, Korea

December 29<sup>th</sup> 2015, Tuesday



Organized by

Materials Theory Group, Yonsei University, Korea

# Contents

## Session A: Nanoparticle

Chlorine with Pt atom: Synergy or Dischord?

*Youngjoo Tak* . . . . . 3

Size Dependent Phase Diagrams of Nickel-Carbon Nanoparticles

*Jiwoo Lee* . . . . . 4

## Session B: Practical Sharing Session

Practical sharing of optical calculations in VASP

*Woosun Jang* . . . . . 5

## Session C: Bulk Oxides

Influence of *xc* functional on thermal-elastic properties of Ceria: A DFT-based Debye-Grüneisen model approach

*Ji-Hwan Lee* . . . . . 6

A DFT Study of the phase transition among polymorphs of MoO<sub>3</sub>

*Jongmin Yun* . . . . . 7

A DFT Study in the Photochemistry of the Metastable *h*-WO<sub>3</sub>

*Yonghyuk Lee* . . . . . 8

## Session D: Complex Bulk

Study of BaZrS<sub>3</sub> and BaZrSe<sub>3</sub> for photovoltaic applications

*Jaeho Yoon* . . . . . 9

Electronic Properties of Single-strand Polyimide as Metal-free Photocatalyst

*Jong-Hun Park* . . . . . 10

Cation Induced Band Level Modulation in Lead-Free Halide Perovskite: Application to Photovoltaic Cell

*Youngkwang Jung* . . . . . 11

**Session E: Surface**

Microfaceting of Cu<sub>2</sub>O and its implications in photochemistry

*Yunjae Lee* . . . . . 12

Phase stability of ZnO(0001)-Zn surfaces in contact with liquid water: A first-principles study

*Su-Hyun Yoo* . . . . . 13

Oxidic copper on the Au(111) surface:A theoretical surface science approach

*Taehun Lee* . . . . . 14

## Chlorine with Pt atom: Synergy or Dischord?

Youngjoo Tak

*Department of Materials Science and Engineering, Yonsei University, Seoul 120-749, Korea*

Platinum is one of the most broadly used catalyst for many chemical reactions (e.g. oxygen reduction reaction). Although its great reactivity, platinum catalysis has not met enthusiastic reception from industry due to its high price. Pt/C catalyst is widely used to come over this problem, but still considered as an imperfect solution because of its poor stability [1,2]. Recently, platinum single-atom catalyst with TiN support has suggested and proved to be stable on the N vacancy site of TiN support under N-lean condition [3]. For synthesis of Pt single atom catalyst, precursor which containing Cl is widely using these days (e.g.  $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ ) and possibility of residual Cl ion on Pt single atom catalyst system is exists. In this work, we present density-functional theory (DFT) study of the influence of chlorine ion on TiN and TiC surface. From here, we will discuss possibility of residual chlorine ion on TiN and TiC surface and how it will influence to stability of Pt on those non-conventional support materials surfaces.

[1] Z. Peng and H. Yang, *Nano Today* **4**, 143 (2009)

[2] B. Avasarala, T. Murray, W. Li and P. Haldar, *J. Mater. Chem.* **19**, 1803 (2009)

[3] R. Q. Zhang, T. H. Lee, B. D. Yu, C. Stampfl and A. Soon, *Phys. Chem. Chem. Phys.* **14**, 16552 (2012)

[4] T. J. Schmidt, U. A. Paulus, H. A. Gasteiger and R. J. Behm, *J. Electroanal. Chem.* **508**, 41 (2001)

## Session A: Nanoparticle [10:30 ~ 10:50]

### Size Dependent Phase Diagrams of Nickel-Carbon Nanoparticles

Jiwoo Lee

*Department of Materials Science and Engineering, Yonsei University, Seoul 120-749, Korea*

Synthesis of nanotubes from solid state nanoparticles, single wall carbon nanotubes (SWNTs), [1] has recently been proposed, and understanding an incorporation of carbon in nanoparticles is addressed especially for typical catalyst nanoparticles like palladium, nickel, or iron. [2-5] In this work, nickel-carbon nanoparticles size up to about 3 nm (807 Ni atoms), in relevant for SWNT growth, are calculated for face centered cubic (fcc, Wulff-shpaed) and icosahedral nickel-carbon nanoparticles to obtain nickel-carbon phase diagram as a function of size, temperature, and carbon chemical potential. It was revealed that nanoparticles melting is strongly favored by carbon incorporation which cause a large downshift of eutectic point as compared to a bulk phase diagram. Also a size dependence of the phase diagram will envision the possibility of a better control on SWNTs and expand to another nanoalloys.

[1] F. Yang *et al.*, *Nature* **510**, 522 (2014)

[2] D. Teschner, J. Borsodi, A. Wootsch, Z. Révay, M. Hävecker, A. Knop-Gericke, S. D. Jackson and R. Schlögl, *Science* **320**, 86 (2008)

[3] A. Rinaldi, J.-P. Tessonnier, M. E. Schuster, R. Blume, F. Girgsdies, Q. Zhang, T. Jacob, S. B. Abd Hamid, D. S. Su and R. Schlögl, *Angew. Chem. Int. Ed.* **50**, 3313 (2011)

[4] R. S. Weatherup *et al.*, *J. Am. Chem. Soc.* **136**, 13698 (2014)

[5] S. Mazzucco, Y. Wang, M. Tanase, M. Picher, K. Li, Z. Wu, S. Irle and R. C. J. Sharma, *Catalysis* **319**, 54 (2014)

## Session B: Practical Sharing Session [10:50 ~ 11:10]

### Practical sharing of optical calculations in VASP

Woosun Jang

*Department of Materials Science and Engineering, Yonsei University, Seoul 120-749, Korea*

In these days, density functional theory (DFT) is known for the most powerful method for condensed matter calculations. The success of DFT is mostly based on the exchange and correlation ( $xc$ ) energy in the local-density (LD) or generalized gradient (GG) approximation. However, in the case of calculating electronic excitation energies of semiconductors and insulators, Kohn-Sham formalism which underlies on the DFT fails.[1,2] In this session, practical examples and basic background concept for accurate excited states calculations will be explained from the simplest approximation such as independent-particle approximation to the complex GW approximation implemented in Vienna *Ab initio* Simulation Package (VASP).[1-5]

[1] M. Gajdoš, K. Hummer, G. Kresse, J. Furthmüller, and F. Bechstedt, *Phys. Rev. B* **73**, 045112 (2006)

[2] F. Fuchs, J. Furthmüller, F. Bechstedt, M. Shishkin, and G. Kresse, *Phys. Rev. B* **76**, 115109 (2007)

[3] G. Kresse and J. Hafner, *Phys. Rev. B* **47**, 558 (1993)

[4] G. Kresse and J. Hafner, *Phys. Rev. B* **49**, 14251 (1994)

[5] G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996)

**Influence of  $xc$  functional on thermal-elastic properties of Ceria: A  
DFT-based Debye-Grüneisen model approach**

Ji-Hwan Lee

*Department of Materials Science and Engineering, Yonsei University, Seoul 120-749, Korea*

Ceria ( $\text{CeO}_{2-x}$ ) is widely studied as a choice electrolyte material for intermediate-temperature ( $\sim 800$  K) solid oxide fuel cells. At this temperature, maintaining its chemical stability and thermal-mechanical integrity of this oxide are of utmost importance. To understand their thermal-elastic properties, we firstly test the influence of various approximations to the density-functional theory (DFT)  $xc$  functionals on specific thermal-elastic properties of both  $\text{CeO}_2$  and  $\text{Ce}_2\text{O}_3$ . Namely, we consider the local-density approximation (LDA), the generalized gradient approximation (GGA-PBE) with and without additional Hubbard  $U$  as applied to the  $4f$  electron of Ce, as well as the recently popularized hybrid functional due to Heyd-Scuseria-Ernzehofer (HSE06). Next, we then couple this to a volume-dependent Debye-Grüneisen model to determine the thermodynamic quantities of ceria at arbitrary temperatures. We find an explicit description of the strong correlation (e.g. via the DFT+ $U$  and hybrid functional approach) is necessary to have a good agreement with experimental values, in contrast to the mean-field treatment in standard  $xc$  approximations (such as LDA or GGA-PBE).

## A DFT Study of the phase transition among polymorphs of MoO<sub>3</sub>

Jongmin Yun

*Department of Materials Science and Engineering, Yonsei University, Seoul 120-749, Korea*

Molybdenum trioxide (MoO<sub>3</sub>) has been a key material for various applications in electronics due to its remarkably high work-function about 6.6 eV and its electronic structure. (e.g. Li battery electrode, electrode surfaces in organic photo-voltaic and organic light emitting diodes (as an anode or hole transfer dopant for MoS<sub>2</sub> devices) etc.) [1,2] Most theoretical investigations about this material have been focused on the orthorhombic phase ( $\alpha$ -MoO<sub>3</sub>), which is known as the most stable one in the room environment. However, it has been started well-known that other phases of MoO<sub>3</sub> are highly dependent on the synthetic route which means it can be also stabilized at the ambient environment.[3] Even, enhanced electrochromic properties of the hexagonal *h*-MoO<sub>3</sub> nanobelts has been introduced in comparison with the conventional stable phase.[4] Therefore investigation the phase transition among the MoO<sub>3</sub> polymorphs are valuable since it can provide a detailed guidance to experiments who wants to synthesis and control the phases. In this work, we present a density-functional theory study of bulk molybdenum trioxide (MoO<sub>3</sub>) polymorphs and examination of the influence of temperature on its thermodynamic stability and its electronic properties.

[1] K. T. Butler, R. C. Otero, John Buckeridge, D. O. Scanlon, E. Bovill, D. Lidzey, and A. Walsh *Appl. Phys. Lett.* **107**, 231605 (2015)

[2] Y. Guo and J. Robertson *Appl. Phys. Lett.* **105**, 222110 (2014)

[3] H.-J. Lunk *et al.*, *Inorg. Chem.* **49**, 9400 (2010)

[4] L. Zheng, Y. Xu, D. Jin, and Y. Xie *Chem. Mater.* **21**, 5681 (2009)



## A DFT Study in the Photochemistry of the Metastable $h$ -WO<sub>3</sub>

Yonghyuk Lee

*Department of Materials Science and Engineering, Yonsei University, Seoul 120-749, Korea*

Tungsten trioxide (WO<sub>3</sub>) is a key material for massive applications in photochemistry. (e.g. smart windows, dye-sensitized solar cells, sensors, water splitting catalysis, etc.) [1] Most investigations about the material have been concentrated on the monoclinic phase ( $\gamma$ -WO<sub>3</sub>), which is the most stable in the room temperature. But, the optical gap of  $\gamma$ -WO<sub>3</sub> is too large for efficient visible light absorption. Therefore, recently, a number of investigations were focused on lowering the band gap of this material. It was revealed that thermodynamically metastable phases exhibit a smaller band gap than  $\gamma$ -WO<sub>3</sub>. [2] In this work, we present a first-principles hybrid density-functional theory investigation of bulk hexagonal tungsten trioxide ( $h$ -WO<sub>3</sub>) and examine the influence of alkali ion intercalation chemistry on its thermodynamic stability as well as its optoelectronic properties. Furthermore, we consider the various orientations and terminations of  $h$ -WO<sub>3</sub> surfaces and address the predicted nanomorphologies under corresponding experimental conditions based on the DFT-derived Gibbs-Wulff polyhedrons. We provide a microscopic perspective for its potential applications in photoreactions by studying the surface energetics and electronic structure.

[1] C. G. Granqvist, *Sol. Energy Mater. Sol. Cells* **60**, 201 (2000)

[2] Y. Ping and G. Galli, *J. Phys. Chem. C* **118**, 6019 (2014)

## Session D: Complex Bulk [13:30 ~ 13:50]

### Study of BaZrS<sub>3</sub> and BaZrSe<sub>3</sub> for photovoltaic applications

Jaeho Yoon

*Department of Materials Science and Engineering, Yonsei University, Seoul 120-749, Korea*

In the perovskite photovoltaic fields, the non-toxic such as lead-free perovskites are in great attention for many researchers. Chalcogenide perovskite is one of the lead-free perovskites that can be used for substitution of organo-metal halide perovskite in photovoltaics.[1] [2] [3] Chalcogenide perovskite such as CaZrSe<sub>3</sub> has an ideal properties for photovoltaics.[4] However, in the meantime, chalcogenide perovskite haven't attract the researchers because oxide perovskites generally have a better properties for photovoltaic applications such as a water resistance or band gap energies. As a result, the study of basic properties of BaZrS<sub>3</sub> and BaZrSe<sub>3</sub> is a good starting point for chalcogenide perovskite photovoltaic applications. In this research, we present density functional theory (DFT) based calculation for BaZrS<sub>3</sub> and BaZrSe<sub>3</sub> and find properties such as the optimized structures, bulk modulus, formation energies, density of states, and band structures.

[1] M. Grätzel, *Nature Materials* **13**, 838 (2014)

[2] A. Kojima, K. Teshima, Y. Shirai and T. Miyasaka, *J. Am. Chem. Soc.* **131**, 6050 (2009)

[3] M. A. Green, A. Ho-Baillie and H. J. Snaith, *Nature Photonics* **8**, 506 (2014)

[4] Y. Sun, M. L. Agiorgousis, P. Zhang and S. Zhang, *Nano Lett.* **15**, 581 (2015)

## Electronic Properties of Single-strand Polyimide as Metal-free Photocatalyst

Jong-Hun Park

*Department of Materials Science and Engineering, Yonsei University, Seoul 120-749, Korea*

In order to substitute fossil fuel energy, there have been many studies about new generation energy. Hydrogen molecule is the one of the alternatives and it can be formed from the water by abundant solar energy in the presence of photocatalyst. Until now the various materials have been explored for the suitable photocatalyst such as  $\text{TiO}_2$ , GaN, ZnO,  $\text{WO}_2$  and even 2D material  $\text{MoS}_2$ . [1-2] In the environmental point of view photocatalytic material, organic materials have been focused on recently. In 2012, polyimide photocatalyst is suggested by Chu *et al.* due to the eco-friendly synthesis without solvent. [3] Despite of the studies, there are many potential materials for polyimide photocatalyst unrevealed. In this study, we explore four polyimide 1D strand (PMDA-ODA, BTDA-ODA, BPDA-ODA, and ODPA-ODA) as candidates for organic photocatalyst. The investigation of the band structure may suggest the probability of the polyimides as metal-free photocatalyst.

[1] K. Maeda and K. Domen, *J. Phys. Chem. Lett.* **1**, 2655 (2010).

[2] Y. Li, Y.-L. Li, C. Araujo, W. Luo and R. Ahuja, *Catal. Sci. Technol.* **3**, 2214 (2013).

[3] S. Chu, Y. Wang, Y. Guo, P. Zhou, H. Yu, L. Luo, F. Kong and Z. Zou, *J. Mater. Chem.* **22**, 15519 (2012)

## Cation Induced Band Level Modulation in Lead-Free Halide Perovskite: Application to Photovoltaic Cell

Youngkwang Jung

*Department of Materials Science and Engineering, Yonsei University, Seoul 120-749, Korea*

CsSnI<sub>3</sub> perovskite has been proposed as a promising lead-free perovskite materials for application to photovoltaic cell these days due to its non-toxicity, suitable band gap, and high electrical conductivity. In spite of these advantages, CsSnI<sub>3</sub> perovskite faced a limitation of inappropriate band level with hole transfer material, spiro-MeOTAD. Recent study reported that electronic band properties of these tin halide perovskites are less affected by electronic structure of cation, but affected by cation induced distortion of tin-iodine octahedron, [SnI<sub>6</sub>], indirectly. In this work, we hypothesize that the distortion might relate to the size of cation and affect to band level of CsSnI<sub>3</sub> perovskite, and investigate this hypothesis with density-functional theory (DFT) calculation by substituting Cs to smaller Rb. Based on PBE of *xc* functional, the calculated structures show more distortion of [SnI<sub>6</sub>] and change of band gap with higher concentration of Rb. In the end, we suggest a novel way to modulate band gap and band level of Cs<sub>1-x</sub>Rb<sub>x</sub>SnI<sub>3</sub> perovskite and prediction of theoretical equilibrium doping concentration as a function of temperature computed by Van't Hoff equation.

## Microfaceting of Cu<sub>2</sub>O and its implications in photochemistry

Yunjae Lee

*Department of Materials Science and Engineering, Yonsei University, Seoul 120-749, Korea*

The high Miller-index microfacets e.g. {211}, {311}, and {522} have been proposed to play a key role in shape-controlled crystal engineering of Cu<sub>2</sub>O polyhedrons for various clean energy applications [1]. These Cu<sub>2</sub>O microcrystals with high Miller-index microfacets are found to have a higher photocatalytic activity than those with octahedra and cube morphologies, and thus suggesting that the catalytically active sites are more abundant on the high Miller-index surfaces. Although much effort has been devoted to the actual synthesis and characterizations of these shaped Cu<sub>2</sub>O nanocrystals with various morphologies, a firm theoretical understanding of these system are currently limited to low Miller-index facets of Cu<sub>2</sub>O [2]. Here, we perform first-principles density-functional theory (DFT) calculations using the Vienna *ab initio* Simulation Package (VASP) to study the surface energetics and electronic structure of these high Miller-index Cu<sub>2</sub>O surfaces, and evaluate their overpotential for water redox reactions on Cu<sub>2</sub>O, in comparison with that for the low Miller-index surfaces.

[1] X. Wang, S. Jiao, D. Wu, Q. Li, J. Zhou, K. Jiang and D. Xu, *Cryst. Eng. Comm* **15**, 1849 (2013)

[2] A. Soon, M. Todorova, B. Delley, and C. Stampfl, *Phys. Rev. B* **75**, 125420 (2007)

**Phase stability of ZnO(0001)-Zn surfaces in contact with liquid water: A first-principles study**

Su-Hyun Yoo

*Max-Planck-Institut fuer Eisenforschung, Max-Planck-Strasse 1, 40237, Duesseldorf, Germany*

Zinc oxide (ZnO) is a wide bandgap semiconductor, which is intensively studied due to its various applications in different fields, such as (photo-)catalysis, protective coating, optoelectronics and others. A polar ZnO(0001) surface is catalytically active, compared to other surfaces. The polar ZnO surface, however, reveals diverse reconstructed phases, such as triangular reconstruction, defects, and adsorption of different species, due to the inherent instability from surface dipoles. Therefore, understanding the impacts of a humid or an aqueous environment on the surface structure is critical in the context of several applications. Focusing on the polar Zn terminated ZnO(0001) surface, we study the stability of surface phases by means of density functional theory (DFT) combining with *ab-initio* atomistic thermodynamics and implicit solvation model (VASPsol) [1]. The constructed surface phase diagram of ZnO under humid and water environment will be compared. The details of calculated solvation energy of various surface phases will be also discussed through electronic structure analysis.

[1] M. Fishman, H. L. Zhuang, K. Mathew, W. Dirschka, and R. G. Hennig, *Phys. Rev. B* **87**, 245402 (2013)

**Oxidic copper on the Au(111) surface: A theoretical surface  
science approach**

Taehun Lee

*Department of Materials Science and Engineering, Yonsei University, Seoul 120-749, Korea*

Recently, via reactive Cu deposition in an oxygen ambience, high quality gold-supported cuprous oxide ( $\text{Cu}_2\text{O}$ ) ultrathin nanofilms [1] have been prepared as a model system to further such catalytic studies. Nonetheless, an accurate atomic picture of these ultrathin  $\text{Cu}_2\text{O}$  nanofilms, which largely depends on its immediate oxygen environment, is currently lacking. In this work, we perform density-functional theory (DFT) calculations using the Vienna ab initio Simulation Package in combination with *ab initio* atomistic thermodynamics [2] to investigate stability of  $\text{Cu}_2\text{O}$  thin films on Au(111) as a function of oxygen chemical potential. Our results indeed show that some of the surface structures suggested in Ref. [1] are energetically more stable than the traditional copper oxide thin film structures on copper substrate, and elucidated the electronic structure of these ultrathin copper oxide films on gold, in comparison with available experimental data.

[1] H. Sträter *et al.*, *J. Phys. Chem. C* **119**, 5975 (2015)

[2] A. Soon *et al.*, *Phys. Rev. B* **73**, 165424 (2006)