Dalton Transactions

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/dalton

Hydrophobic and antioxydant effects in In, Sn, and Sb based two dimensional materials†

Keisuke Takahashi[a] **and Lauren Takahashi***[b]

Received Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
First published on the web Xth XXXXXXXXXX 200X
DOI: 10.1039/b000000x

Hydrophobic and antioxydant effects of two dimensional materials Sn, SnSb, InSb, and InSn are investigated with the implementation of first principle calculations. The stable atomic configurations of two dimensional SnSb, InSb, and InSn are determined where the structures are buckled. Adsorption of water and oxygen molecules over such surfaces reveals that SnSb (with Sb as the top surface) particularly has an outstanding hydrophobic effect while InSb (with Sb as the top surface) has a high antioxydant effect. The physical origin rests on the charge transfer where electrons are transfered from O to H in H_2O, resulting in an increase of polar states between H and O, thereby leading to weak H_2O adsorption on SnSb. On the other hand, there is no charge transfer between O_2 and InSb(with Sb as the top surface) while O_2 adsorption is involved with large electron transfer from the surface to oxygen in other surfaces. Thus, two dimensional SnSb and InSb offer hydrophobic and antioxydant properties, respectively, where such properties would be appreciated for designing surface coatings and electric circuit.

Recognition and exploration of two dimensional materials have constantly brought forth unexpected scientific phenomenon since the discovery of graphene[1,2]. The unusual physical and chemical properties of graphene have also led towards further investigations of potential two dimensional materials[3,4]. In particular, two dimensional tin, named stanene, theoretically demonstrates unique physical and chemical properties where stanene is found to be a topological insulator and have the ability to decompose nitric and sulfer oxides at room temperature[5,6]. Experimental techniques have quickly accomplished the synthesis of stanene with handling the epitaxial growth[7]. The unique story of stanene indicates the importance of exploring other possible two dimensional materials.

Theoretical research has provided insight for synthesizing other potential two dimensional materials through manipulation of the boron and pnictogen groups such as two dimensional BN and AlP[8,9]. Since this approach has proved effective in the cases of BN as well as AlP, neighboring elements of Sn, In and Sb, should be able to form together and form InSb. In general, indium and antimony have shown hydrophobic effects with relatively good tolerance against oxygen[10,11]. Given these properties, manupulating Sn, In, and Sb as two dimensional materials could prove to be useful in designing hydrophobic and antioxydant materials.

Undiscovered structures and bond types of two dimensional SnSb, InSb, and InSn are explored based on first principle calculations. Adsorption of water and oxygen molecules over two dimensional Sn, SnSb, InSb, and InSn are investigated in order to reveal possible hydrophobic and antioxydant effects.

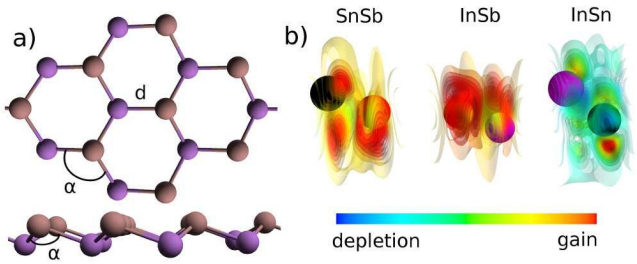


Fig. 1 (a) Atomic configuration of Sn, SnSb, InSb, and InSn where the bond angle and bond distance are indicated as α and *d*, respectively. Corresponding α and *d* for Sn, SnSb, InSb, and InSn are listed in Table (1). (b)Charge density difference of SnSb, InSb, and InSn where red(blue) represents electron gain(depletion). Atomic color code: black-Sn, Purple-In, Red-Sb.

The first principle calculations based on the grid-based projector-augmented wave (GPAW) is implemented with the exchange correlation of Perdew-Burke-Ernzerhof and spin polarization[12,13]. The supercells of two dimensional Sn, InSn, SnSb, and InSb of (3x3) and bulk Sn(100), In(100), and Sb(100) of (3x3) are constructed with periodic boundary conditions where the the special K point of (8x8x1) is applied[14]. Electron transfers are calculated based on the Bader charge analysis[15,16]. Adsorption energies (E_{ad}) of H_2O and O_2 are calculated based on (1):

† Electronic Supplementary Information (ESI) available:

[a] *Graduate School of Engineering, Hokkaido University, N-13, W-8, Sapporo 060-8628, Japan. E-mail: keisuke.takahashi@eng.hokudai.ac.jp*
[b] *Freelance Researcher, Central Ward, Sapporo 064, Japan.*

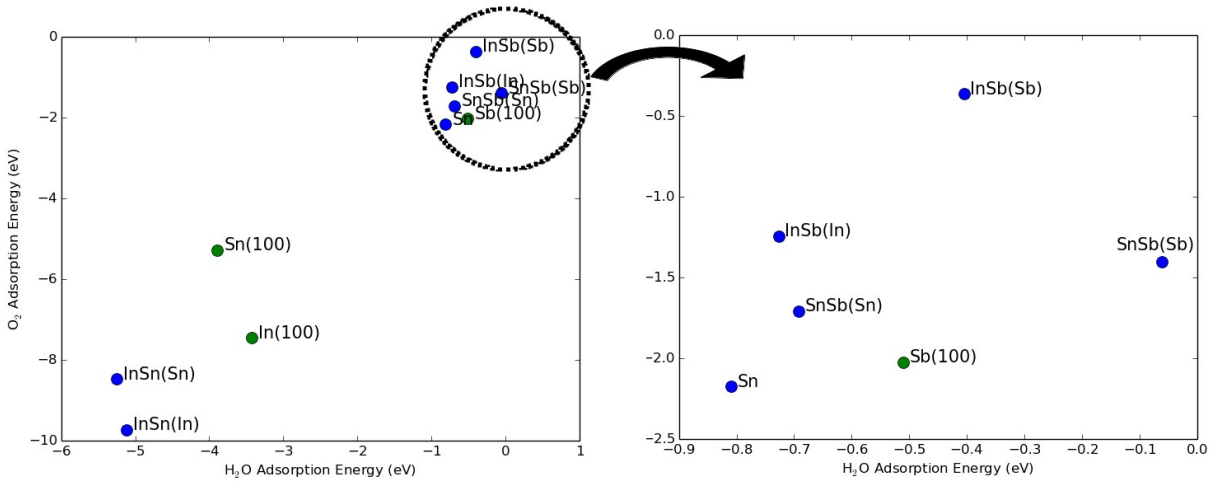


Fig. 2 Adsorption energies of H_2O and O_2 over two dimensional Sn, SnSb, InSb, InSn, and bulk Sn(100), In(100), and Sb(100). Note that elements between parentheses (for instance, Sn in InSn(Sn) are the elements in which the surface of that material are made of.)

$$E_{ad} = -(E[Sur+Ad] - E[Sur] - E[H_2O(O_2)]) \quad (1)$$

The structure of two dimensional SnSb, InSb, and InSn are investigated using first principle calculations. Structural data is collected in Figure 1 and Table 1. The lattice constant of InSb is calculated to be 4.68 Å which is slightly longer than Sn, 4.62 Å while the bond lengths of In-Sb and Sn-Sn are the same with a value of 2.89 Å. The difference between the lattice constants is considered to be due to the bond type between In-Sb and Sn-Sn. The bond type of Sn is calculated to be a weak covalent bond[6] while there is an ionic bond based on electron transfers involved for In-Sb, resulting in different angles as shown in Figure 1 and Table 1. In the same fashion, the lattice constant of InSb is calculated to be 4.57 Å with a slightly larger bond length compared to the SnSb case while both cases of InSb and SnSb are involved with electron transfers. The slightly large bond length of SnSb is due to 0.1 less electrons transferred compared to InSb, resulting in slight weak ionic bonding. The lattice constant and angle of InSn are particularly small at 4.28 Å and 85.8° respectively, while the bond length is large at 3.15 Å. Figure 1(b) indicates that the bond type of InSn is a weak covalent bond, similar to the Sn case. This implies that the reactivities of InSn are expected to be high for certain molecules based on high reactivities of Sn against NO_x,CO_x, and SO_x.

Adsorption of H_2O and O_2 over Sn, SnSb, InSb, InSn, and bulk Sn(100), In(100), and Sb(100) is investigated where two different top surfaces are considered for the cases of SnSb, InSb, and InSn. Adsorption energies are collected in Figure 2. H_2O and O_2 adsorption energies and geometry information

	Lattice	Bond length	Angle	Sn	Sn	In	Sb
Sn	4.62[6]	2.89[6]	106[6]	0	0	N/A	N/A
SnSb	4.57	3.00	100	0.3	N/A	N/A	-0.3
InSb	4.68	2.89	108	N/A	N/A	0.4	-0.4
InSn	4.28	3.15	85.8	N/A	0.1	-0.1	N/A

Table 1 The lattice constant (Å), bond length(Å), Angle(°), and charge tranfer(electron) of two dimensional- Sn, InSn, SnSb, and InSb.

are listed in supplementary information. In particular, Figure 2 demonstrates low adsorption energies of H_2O and O_2 in two dimensional materials InSb(where Sb is the top surface), Sn, InSb(In), SnSb(Sn), SnSb(Sn) and bulk Sn(100) where SnSb (Sb as top surface) has exceptionally low H_2O adsorption energy of -0.06 eV while InSb(Sb as top surface) has low O_2 adsorption energy of -0.36eV. -0.06 eV of H_2O adsorption over SnSb(Sb) is exceptionally low compared to the H_2O over common metal surfaces where H_2O adsorption is reported to be 0.1 eV to 0.4eV over Au, Pt, and Ru[17]. The key element for hydrophobic and antioxidant effects is considered to be Sb based on Figure 2. Furthermore, H_2O and O_2 adsorption energies on two dimensional structures are generally much smaller than those on bulk surfaces as shown in Figure 2.

The physical origin of low H_2O and O_2 adsorption energy over SnSb(Sb) and InSb(Sb) relies on the complex of electron transfers. Upon the adsorption of H_2O on SnSb(Sb), O atom in H_2O released 0.1 electrons while each H atom gained 0.02 electrons. As a result, the polar state of H and O in H_2O becomes slightly stronger, leading to a stronger bond between H and O, and ,therefore, low adsorption energies is induced. In the case of low O_2 adsorption energy in SnSb(Sb), elec-

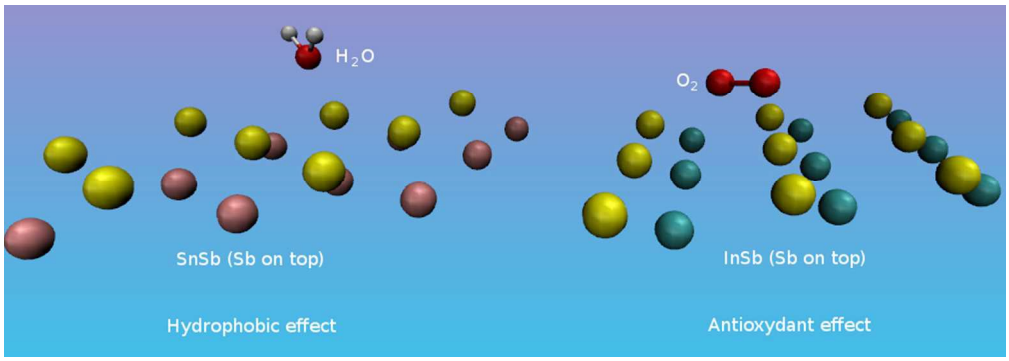
tron transfer is not involved between InSb(Sb) and O_2. When strong oxydation occurs in cases such as InSn, each of the O atoms in O_2 is negatively charged by 1.0 electron from the InSn surface. Therefore, the electron transfers are the key component to explaining the hydrophobic and antioxidant effects on such surfaces.

In conclusion, first principle calculations reveal the stable atomic configurations and bond types of two dimensional SnSb, InSb, and InSn. Hydrophobic and antioxydant effects on such surfaces are investigated where SnSb(Sb) and InSb(Sb) result in exceptionally low H_2O and O adsorption energies, respectively. The physical origin of such effects rest on the complex of charge transfer. The O atom in H_2O over SnSb(Sb) releases 0.1 electrons while the H in H_2O gained 0.02 electron, resulting in the increase of polar states between H and O,and thereby leading towards low H_2 adsorption energy. On the other hand, the nature of ionic bond in InSb(Sb) results in no electron transfer between O_2 and InSb(Sb), resulting in low O_2 adsorption. Such phenomena are potentially important for applications in designing surface coatings and electric circuits.

CPU time is funded by the Japan Society for the Promotion of Science. Computational work is supported in part by Hokkaido university academic cloud,information initiative center, Hokkaido University, Sapporo, Japan.

References

1 K. Novoselov, D. Jiang, F. Schedin, T. Booth, V. Khotkevich, S. Morozov, and A. Geim, Proceedings of the National Academy of Sciences of the United States of America **102**, 10451 (2005).
2 A. K. Geim and K. S. Novoselov, Nature materials **6**, 183 (2007).
3 S. Z. Butler, S. M. Hollen, L. Cao, Y. Cui, J. A. Gupta, H. R. Gutierrez, T. F. Heinz, S. S. Hong, J. Huang, A. F. Ismach, *et al.*, ACS nano **7**, 2898 (2013).
4 M. Xu, T. Liang, M. Shi, and H. Chen, Chemical reviews **113**, 3766 (2013).
5 Y. Xu, B. Yan, H.-J. Zhang, J. Wang, G. Xu, P. Tang, W. Duan, and S.-C. Zhang, Physical review letters **111**, 136804 (2013).
6 L. Takahashi and K. Takahashi, Physical Chemistry Chemical Physics **17**, 21394 (2015).
7 F.-f. Zhu, W.-j. Chen, Y. Xu, C.-l. Gao, D.-d. Guan, C.-h. Liu, D. Qian, S.-C. Zhang, and J.-f. Jia, Nature materials **14**, 1020 (2015).
8 H. L. Zhuang, A. K. Singh, and R. G. Hennig, Physical Review B **87**, 165415 (2013).
9 A. K. Singh, H. L. Zhuang, and R. G. Hennig, Physical Review B **89**, 245431 (2014).
10 T.-P. Loh and G.-L. Chua, Chemical communications , 2739 (2006).
11 J. Shan, A. Chakradhar, Z. Yu, and U. Burghaus, Chemical Physics Letters **517**, 46 (2011).
12 J. Mortensen, L. Hansen, and K. Jacobsen, Physical Review B **71**, 035109 (2005).
13 J. P. Perdew, K. Burke, and M. Ernzerhof, Physical review letters **77**, 3865 (1996).
14 H. J. Monkhorst and J. D. Pack, Physical Review B **13**, 5188 (1976).
15 E. Sanville, S. D. Kenny, R. Smith, and G. Henkelman, Journal of computational chemistry **28**, 899 (2007).
16 G. Henkelman, A. Arnaldsson, and H. Jónsson, Computational Materials Science **36**, 354 (2006).
17 S. Meng, E. Wang, and S. Gao, Physical Review B **69**, 195404 (2004).



85x29mm (300 x 300 DPI)