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Low temperature pollutant trapping and dissociation over two-dimensional tin[†]

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Newly discovered two-dimensional tin, named stanene, has been theoretically predicted and found to have unique electronic properties. The structure of stanene is found to have a buckled structure which could be a key structure against chemical reactivity. Hence, the reactivity of stanene against key air pollutants NO, NO$_2$, SO, SO$_2$, CO, and CO$_2$ is investigated within first principle calculations. The results found that stanene is reactive against those air pollutants. Furthermore, the dissociation activation energies of those pollutants over stanene are lower than previous reported catalysts. The physical origin of low dissociation barriers rests in the charge transfer from stanene to those pollutants, resulting in bond weakening. Hence, one can predict that unique reactivities of stanene offers low temperature trapping and dissociation of air pollutants.

The discovery of graphene has lead to the rise of two dimensional materials, opening a new era of material sciences[1,2]. Graphene particularly possesses unique properties that are useful towards applications in filtering water and various gases due to its high surface area-to-volume ratio, stability, and flexibility[3–5]. The possibility of synthesizing other two dimensional materials has led researchers towards discovering other two-dimensional materials outside of graphene[6,7]. In particular, boron nitride has proven to be particularly effective in cleaning up spills, solvents, and dyes present in water and is a potential alternative to current cleanup measures[8]. Because of the unique properties and high surface of two dimensional materials, one can predict that such materials could also trap air pollution if the materials are reactive against them.

Stanene is the theoretically-predicted two dimensional Sn material which is predicted to possess outstanding electronic properties[9,10]. The structure of stanene has a buckled structure rather than a flat structure[11]. Buckled graphene is reported to be reactive against gasses, suggesting that stanene itself could also be reactive against gas molecules due to its buckled surface[12]. Given graphene's gas permeability and ability to fil-

ter various gases[3,4] and tin's role in gas detection, one can predict that stanene may also prove useful in trapping undesirable gases. Here, the reactivity of stanene against key air pollutions- namely, sulfur, carbon and nitric oxides- is investigated using density functional theory.

The grid-based projector-augmented wave (GPAW) method within the density functional theory is implemented along the spin polarization[13,14]. The exchange correlation of Perdew-Burke-Ernzerhof and the special K point of (4x4x1) is applied within the periodic boundary conditions[15,16]. The supercell of (3x3x3) of stanene is used. Bader charge analysis and the nudged elastic band method are implemented for charge transfer analysis and activation barrier calculations, respectively[17–19]. Note that negative adsorption energy indicates an exothermic reaction.
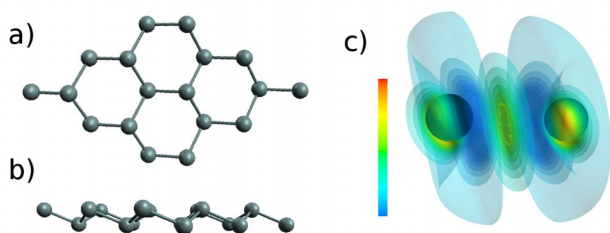

Fig. 1 The structure of stanene. (a) Top view (b) Side view (c) Charge density difference map of stanene where blue and red indicates electron depletion and gain, respectively, while green indicates a neutral state.

The structure of stanene is investigated. The calculated stanene is shown in Figure 1 where (a) and (b) show its structure and (c) is its charge density difference map. The lattice constant and Sn-Sn bond length is calculated to be a=b=4.62 Å and 2.85 Å, respectively, which demonstrates good agreement with previous theoretical work[11]. Zhu et al. has experimentally synthesized stanene using the epitaxial growth technique over Bi$_2$Te$_3$(111) where the lattice constant is found to be 4.38 Å, demonstrating that slight shrinkage of stanene should be considered when deposited onto a substrate in comparison to free standing stanene[20]. The structure of stanene is buckled

in a fashion similar to silicene as shown in Figure 1(b)[21]. The charge density difference map shown in Figure 1(c) indicates that the bond type of Sn-Sn bond is a weak covalent bond where the Bader analysis shows no charge transfer between the Sn-Sn bond.

The adsorption and dissociation barriers of key air pollutions NO, NO_2, SO, SO_2, CO, and CO_2 over stanene are performed. Adsorption of NO elongates the bond length of gas phase NO, 1.37 Å to 1.54 Å, over the stanene where N and O are adsorbed at the bridge and top sites of Sn. The NO dissociation barrier is calculated to be 0.18 eV, which is comparitive to values reported for NO dissociation over corrugated Ru and is lower than the 1.28 eV reported for a flat Ru surface[22]. Elongation and a low activation barrier are explained by the charge transfer where the Bader analysis reveals that N and O are both negatively charged by 0.8 and 0.5 electrons from stanene, resulting in negative-negative repulsion. The addition of an extra oxygen atom has shown to have an increase on the adsorption energy as well as a decrease in the dissociation barrier, which are reported to be -2.54 eV and 0.07 eV, respectively. Elongation of the NO bond is also observed in NO_2 adsorption over stanene where the bond lengths of N-O in NO_2 is elongated by 0.07 Å and 0.1 Å compared to gas phase NO_2. Unlike the case of NO, the O atoms of NO_2 are found to be at the bridge site of stanene. Charge analysis also indicates that N is positively charged by 0.1 electrons and O is negatively charged by 0.7 electrons, suggesting that the bond between N and O atoms is weakened.

Adsorption of SO onto stanene elongates the S-O bond length from 1.77 Å of gas phase to 1.97 Å. Charge transfer shows negative-negative repulsion similar to NO adsorption over stanene where S is negatively charged by 0.7 electrons while O is negatively charged by 0.8 electrons. As a result, negative-negative repulsion is induced between S and O in SO over stanene. Thus, the dissociation activation barrier of SO over stanene is calculated to be 0.17 eV. The adsorption energy of SO_2 over stanene is calculated to be -3.06 eV, the lowest among this work. The S atom in SO_2 over stanene is positively charged by 0.4 electrons while the S atom in gas phase SO_2 is positively charged by 0.9 electrons. O atoms in SO_2 on stanene are negatively charged by 0.7 electrons while the O atoms in gas phase SO_2 are negatively charged by 0.5 electrons, suggesting that O atoms are receiving electrons from Sn atoms once adsorption occurs. This implies that the S-O bond is weakened over stanene resulting in the dissociation activation barrier of 0.29 eV, which is lower than previously-reported values of 0.50 eV, 0.56 eV, and 1.58 eV[23]. Given the low dissociation barriers, using stanene to capture and dissociate sulfur oxides may be a useful alternative to the Claus and Stretford processes currently used to desulfurize gas.

Adsorption energy of CO is the highest of all tested systems with a value of -1.20 eV. The CO bond length is slightly

elongated from gas phase CO from 1.32 Å to 1.42 Å. Charge analysis shows that there is no change of charge state between the O atom on stanene and the gas phase O while O atoms are both negatively charged by 0.8 electrons. However, C is negatively charged by 0.2 electrons, resulting in the slight negative-negative repulsion. The dissociation barrier is calculated to be 0.19 eV which is lower than previously reported dissociation energies[24,25]. Thus, stanene could potentially assist methanation in the Fischer-Tropsch process. Adsorption of CO_2 over stanene also elongated the C-O bond length from 1.34 Å of gas phase to 1.44 Å. The Bader analysis indicates that C in CO_2 over stanene is positively charged by 0.4 electrons while C in gas phase CO_2 is positively charged by 1.3 electrons. Meanwhile, O atoms are negatively charged by 0.6 electrons as gas-phase and are negatively charged by 0.8 electrons upon adsorption. This suggests that the bond strength of C-O in CO_2 over stanene is slightly weakened, resulting in the higher dissociation activation barrier of 0.62 eV compared to those found for the sulfur and nitric oxides.
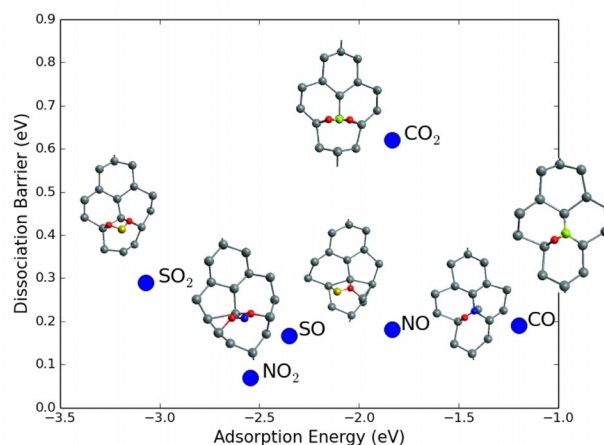

Fig. 2 Adsorption energy and dissociation activation barriers of NO, NO_2, SO, SO_2, CO, and CO_2 over stanene. Atom colors are as follows: Teal-Sn, Red-O, Yellow-S, Blue-N, Green-C.

The overall trend of NO, NO_2, SO, SO_2, CO, and CO_2 over stanene is shown in Figure 2. Figure 2 shows that stanene is particularly effective in adsorbing and dissociating the sulfur and nitric based oxides. This suggests that stanene can be used as a trap device for sulfur and nitric based oxide molecules. Furthermore, these molecules can be decomposed over stanene at low temperature. In the case of carbon based oxides, the adsorption energies are slightly higher than those found in the sulfur and nitric cases. However, the CO and CO_2 adsorption would occur in an exothermic manner and the dissociation activation barrier is still lower than previous reported works, showing that stanene can be potentially used

for the methanation process. Thus, stanene shows outstanding properties for trapping air pollution as well as low temperature decomposition of those pollutants.

The reactivity of stanene for trapping and dissociating six common air pollutants was investigated using first principle calculations. The stable structure of stanene is found to be buckled. Calculations reveal that all six pollutants were trapped over stanene with low adsorption energies. In addition, the dissociation activation barriers of those pollutants are exceptionally low compared to previously reported catalysts. The physical origin of low dissociation activation barriers rests on charge transfer from stanene to those pollutants resulting in bond weakening. The results potentially enable applications in low temperature air pollution trapping where dissociation of pollutants are also predicted to occur at low temperature.

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