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Surface states—the electronic states emerging as a solid material terminates at a surface—are usually vulnerable to contaminations and defects. The robust topological surface state(s) (TSS) on the three-dimensional topological insulators provide a perfect platform for exploiting surface states in less stringent environments. Employing first-principles density functional theory calculations, we demonstrate that the TSS can play a vital role in facilitating surface reactions by serving as an effective electron bath. We use CO oxidation on gold-covered Bi_2Se_3 as a prototype example, and show that the robust TSS can significantly enhance the adsorption energy of both CO and O_2 molecules, by promoting different directions of static electron transfer. The concept of TSS as an electron bath may lead to new design principles beyond the conventional d-band theory of heterogeneous catalysis.

Surface states [1, 2] can be present in many systems, e.g., the free-electron like states on the (111) surfaces of noble metals [3], and the dangling bond derived states on semiconductor surfaces [4]. Aside from their spatial proximity, the sp- or d-band derived surface states can be located at or near the Fermi level (E_F) in energy space; consequently they can significantly influence the physical and chemical processes happening at the surfaces [5–8]. However, since they arise as a result of the different bonding environment at the surface from the bulk [1], normal surface states are easily destroyed by local modifications at the surfaces, e.g., presence of impurities, surface defects, surface reconstruction, or a change in the surface termination or orientation. This fundamental limitation has prohibited systematic studies of the potential role of surface states in surface reactions and catalysis, especially in more realistic environments.

In contrast, the exotic metallic TSS of the recently discovered three-dimensional topological insulators (3DTI) [9–12] are exceptionally robust compared to conventional surface states. The TSS arise from the non-trivial topology of the electron bands of the 3DTI, and their persistence is protected by time-reversal symmetry. Therefore, the TSS are insensitive to the structural details of the surface [13, 14], and will persist as long as the bulk band gap embodying the TSS remains open. The robust TSS thus provides a perfect platform for investigating the catalytic role of surface states in less constrained environments.

In our study, we focus on CO oxidation by supported Au films, a prototype system of fundamental and practical importance in heterogeneous catalysis [15–18]. The use of the 3DTI Bi_2Se_3 [19, 20] as the substrate, instead of conventional oxides such as TiO_2 or MgO, is to introduce additional surface electron states (the TSS) at E_F. As shown recently for the case of metal-induced semi-conductor surface reconstruction [21], such extra states may serve as an electron bath to significantly modify the bonding configurations on the surface through proper static electron transfer.

Our density functional calculations are carried out using the Vienna *ab initio* simulation package (VASP) [22] with PAW potentials [23, 24] and the generalized gradient approximation (PBE-GGA) [25] for exchange-correlation functional. The lattice constants of Bi_2Se_3 are adopted from experiments. The generic Bi_2Se_3 substrate is modeled by a slab of 15 atomic layers or 3 quintuple layers (QL), and a Bi-terminated substrate is realized by removing one outermost Se layer. The vacuum layers are over 20 Å thick to ensure decoupling between neighboring slabs. During relaxation, atoms in the lower 11 atomic layers are fixed in their respective bulk positions, and all the other atoms are allowed to relax until the forces on them are smaller than 0.01 eV/Å. A 7×7×1 k-point mesh is used for the 1×1 surface unit cell, and 3×3×1 for the 2×2 surface unit cell [26].

Crystalline Bi_2Se_3 has rhombohedral structure and its unit cell is composed of 3 weakly coupled QL, each of which comprises of 5 alternating Bi and Se layers in a sequence Se-Bi-Se-Bi-Se [19, 20]. The naturally cleaved surface is therefore the Se surface. In Fig. 1 (a) we plot the band structure around E_F of a naturally cleaved 3 QL Bi_2Se_3 film. The surface states in the bulk band gap ($\sim$0.3 eV) have close to linear dispersion near E_F. This single "Dirac-cone" like band structure is a distinctive feature of the TSS of Bi_2Se_3 [19, 20]. The small gap ($\sim$50 meV) opened at the Dirac point is due to the coupling between the two degenerate TSS on the two surfaces of a very thin 3DTI film [27].

We use the Bi-terminated surface of Bi_2Se_3, to which Au binds more strongly than the naturally cleaved Se surface [28], to support Au atoms without formation of
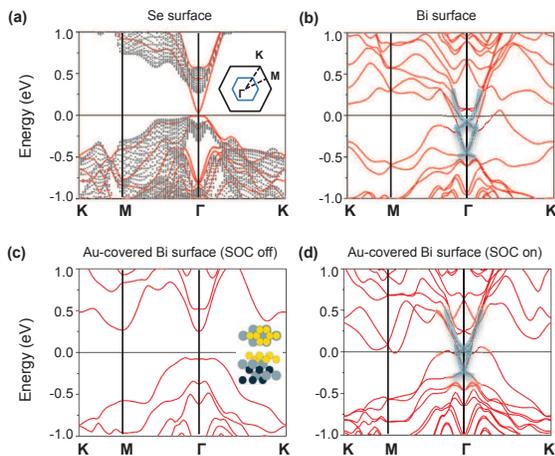
FIG. 1: (color online). (a) Band structure of a 3 QL Bi_2Se_3 film, where the shaded area is the bulk band structure projected to the 2D Brillouin zone. The inset shows the shape of the 2D Brillouin zone for different surface unit cells (Black solid lines-1×1; blue solid lines-2×2). (b) Band structure of a Bi-terminated Bi_2Se_3 film. (c) and (d) Band structures of 2 ML Au deposited on the Bi-terminated surface without and with SOC, respectively. In (b) and (d) the TSS are highlighted by the transparent blue lines. The inset in (c) shows the top and side views of the structure (only top 4 atomic layers of Bi_2Se_3 are shown). Yellow balls-Au; light blue balls-Bi; dark blue balls-Se.

3D Au clusters [17]. Experimentally it is possible to intentionally introduce a large amount of Se vacancies on the surfaces of Bi_2Se_3 or eventually form a complete Bi-terminated surface, due to the large vapor pressure difference between Bi and Se [27]. We therefore can use the ideal Bi-terminated surface in the present proof-of-principle study. The band structure of the Bi-terminated film is shown in Fig. 1 (b). The two TSS Dirac bands still robustly persist and shift below E_F, agreeing with experiments [13, 19]. Additionally, the degeneracy of the two Dirac bands is lifted, of which the upper and lower bands correspond to the TSS at the upper (Bi-terminated) and lower (Se-terminated) surface, respectively.

We choose 2 monolayers (ML) of Au deposited on the Bi surface of the Bi_2Se_3 film (Fig. 1 (c) inset) as a model system because of its optimal stability [28] for subsequent calculations. Here 1 ML is defined to be the same number of atoms as that in each atomic layer of Bi_2Se_3, which is equal to 0.48 times the atom density in a (111) layer of bulk Au. Figs. 1 (c) and (d) show the band structures of the Au-covered Bi_2Se_3 film without and with spin-orbit coupling (SOC), respectively. Two TSS Dirac bands emerge only when the SOC is switched on, confirming that the TSS indeed originates from the SOC of the bulk states [9, 10]. This observation allows us to conveniently isolate the effects of the TSS by comparative studies with and without SOC. The shape of the two

TSS bands near the Γ point closely resembles that of the TSS in Fig. 1 (b) for the Bi-terminated Bi_2Se_3 film despite the slight shift in their relative positions in energy. Therefore the TSS survives even if the Bi_2Se_3 surface is completely buried under the 2 ML Au film.

The CO binding energies on the model system with and without SOC, calculated as $\Delta E = E_{adsorbate+substrate} - E_{adsorbate} - E_{substrate}$, are listed in Table I. With SOC, the binding energy is considerably enhanced by 0.2 eV compared to that without SOC, accompanied by a decrease of the C-Au bond length from 2.029 Å to 1.981 Å. The enhanced CO binding with SOC is due to the static electron transfer facilitated by the TSS. To see this effect we first compare the local density of states (LDOS) on the C atom of an adsorbed CO with and without SOC, shown in Fig. 2 (a). The antibonding $2\pi^*$ states shift to higher energies with SOC, indicating decreased electron occupation, and hence enhanced CO-Au binding [29, 30]. On the other hand, from Fig. 2 (c), the top Dirac band, corresponding to the TSS on the Au-deposited Bi-terminated surface, shifts to lower energy after the adsorption of CO, indicating increased electron occupation. Taken together, net electrons are transferred to the TSS serving as an electron bath when CO is adsorbed on the surface.

TABLE I: Binding energies (in eV) of CO and O_2 on three comparative substrates. (1) 2 ML Au on Bi-terminated Bi_2Se_3, (2) freestanding 2 ML Au fixed in the same geometry as in (1), and (3) (unreconstructed) Au(111) surface. The CO/O_2 coverage is 1/4 ML in (1) and (2), and 1/16 ML in (3). The geometries of adsorbed CO and O2 are shown in Figs. 2 (e) and (f), respectively.

		(1) Au-Bi_2Se_3	(2) 2 ML Au	(3) Au(111)
CO	SOC	0.49	0.95	0.30
	No SOC	0.29	0.92	0.27
O_2	SOC	0.23	0.52	<0.01
	No SOC	0.07	0.49	<0.01

The enhanced CO binding with SOC is not due to Au, though Au does have large SOC. To see this we consider two comparative cases: One is fixing the 2 ML Au film in vacuum with the Bi_2Se_3 substrate removed; the other is the unreconstructed Au(111) surface. The Au(111) surface is modeled by a 4 layer slab, each layer comprising of 16 Au atoms, with the lower 2 layers fixed. From Table I, the CO binding energy differences with and without SOC are about one order of magnitude smaller (~0.03 eV) in these two latter cases. We also note that with SOC the CO binding energy on the Au-Bi_2Se_3 system is much larger than that on Au(111). Based on these results, we conclude that the TSS of the underlying Bi_2Se_3 enhance the CO binding by accepting the electrons that otherwise would have been transferred to the antibonding states of the CO-Au system.
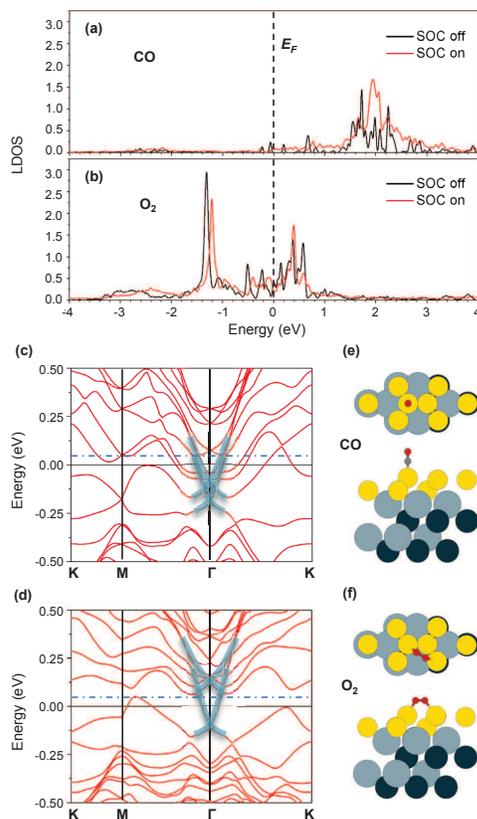
Next we show that the TSS as an electron bath can

decreased spin splitting in the O_2 orbitals. Meanwhile, the O-O bond length increases from 1.289 Å without SOC to 1.299 Å with SOC. The increased electron occupation of the $2\pi^*$ states upon switching on SOC is not easily visible from Fig. 2 (b), but is confirmed by the calculated increase in the relative spectral weight of the $2\pi^*$ DOS below E_F, equal to 0.56 with SOC and 0.55 without SOC. This difference is roughly equal to 0.04 e per O_2 molecule, originated from the TSS. On the other hand, from Fig. 2 (d), the top TSS Dirac band shifts upward compared to that without O_2 adsorption, indicating that electrons are transferred out of the TSS. Therefore, rather than accepting electrons as in the case of CO, the TSS now donates electrons and promotes O_2 toward dissociative adsorption on Au. Moreover, the adsorption energy of O_2 is now comparable to that of CO with a moderate strength, which is a desirable feature for easier reaction and high catalytic activity.

In studying adsorption of molecules on transition metal surfaces, the prevailing theoretical framework has been the d-band theory, according to which the chemical activity of a metal substrate is correlated with the position of its d-band center (E_d) in the energy spectrum [29, 30]. Specifically the closer E_d of the metal substrate to E_F, the stronger molecular adsorbates bind to the substrate. A major contribution to the energy gain as E_d shifts up toward E_F is from the decreased filling of the adsorbate's antibonding states as they are "pushed away" from E_F by the d bands. To see whether our results can be explained independently by the d-band theory, we have calculated E_d of Au in the top layer of the 2 ML Au film [Figs. 3 (a) and (b)] as

$$E_d = \frac{\int_{-\infty}^{\infty} PDOS_d(E) \times (E - E_F)\, \mathrm{d}E}{\int_{-\infty}^{\infty} PDOS_d(E)\, \mathrm{d}E}, \tag{1}$$

where $PDOS_d$ is the density of states projected to the d orbital of Au. We find that, in the present case, E_d actually shifts down away from E_F by 0.21 eV (from -2.68 eV to -2.89 eV) after switching on SOC, and the shift is even larger than that of the freestanding 2 ML Au film, which is 0.12 eV to the same direction (from -2.57 eV to -2.69 eV). These findings unambiguously rule out the d-band theory to be mainly operative in the present systems.

An implicit assumption of the d-band theory is that the sp states around E_F do not differ much among different systems. However, our present study offers a striking and unique counter example to this assumption. In particular, since these TSS are gapless and not completely filled, they can readily donate or accept electrons in order to lower the total energy upon molecular adsorption [see illustrations in Figs. 3 (c-e)]. Such sp-band derived states near E_F, either due to extrinsic effects such as the 3DTI substrate studied here or associated with the transition metals themselves, can play a prominent role
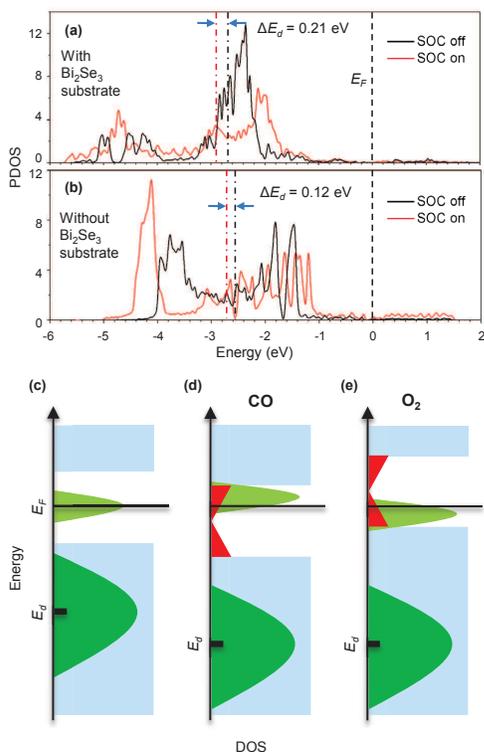

FIG. 2: (color online). (a) and (b) LDOS on the C atom of CO, and one O atom of O_2, featuring the energy range corresponding to the $2\pi^*$ states of CO and O_2, respectively. (c) and (d) Band structures of the CO and O_2 adsorbed 2 ML Au-Bi_2Se_3 film, shown in a reduced Brillouin zone corresponding to the 2×2 surface unit cell (Fig. 1 (a) inset). The TSS bands are highlighted by the transparent blue lines. The blue dot-dash lines indicate the position of the upper Dirac point in Fig. 1 (d). The upper and lower panels in (e) and (f) are the top and side views of the atomic structures. Small red balls-O; small gray balls-C; yellow balls-Au; light blue balls-Bi; dark blue balls-Se.

also enhance the adsorption of O_2, but by invoking a different direction of static electron transfer. On the Au-Bi_2Se_3 substrate, O_2 binding energy increases by 0.16 eV with SOC, which is also much larger than that on the freestanding Au film or Au(111) surface (Table I). The LDOS on one O atom of O_2 is shown in Fig. 2 (b). The two groups of peaks below and above E_F correspond to the spin-up and spin-down antibonding $2\pi^*$ states, respectively [31]. As the half-filled $2\pi^*$ states hybridize with the Au d states, more electrons will be transferred to the $2\pi^*$ states and promote O_2 toward dissociation [31, 32]. At the same time, the spin splitting of the $2\pi^*$ states will decrease due to the weakened O-O bond. In Fig. 2 (b), both groups of the spin-splitted peaks shift toward E_F after turning on SOC, indicating

FIG. 3: (color online). (a) and (b) PDOS of an Au atom in the top layer of the 2 ML Au film with and without Bi_2Se_3 substrate, respectively. In (b) the Au film is fixed in space. The red and black dot-dash lines indicate the positions of E_d with and without SOC, respectively. (c-e) Illustration of the role of the TSS in molecular adsorption. Blue-valence and conduction bands of the 3DTI support; light green-antibonding states of adsorbed molecules; red-TSS; dark green-metal d bands. (c) Without the TSS, the support will not be involved in the static electron transfer. (d) and (e) With the TSS, electrons of the molecule-metal system can be transferred either to or from the partially filled metallic surface states, depending on which way can lower the total energy.

in surface reactivity, especially for late transition metals with deeper d bands. Furthermore, the delocalized sp surface states may also help to smooth the energy profile of the surface and lower the diffusion and reaction barriers of the adsorbed molecules [5, 6], an intriguing aspect worth future investigations. The present study indicates manipulation of the sp surface states may be complementary to the guiding principles from d-band theory in searching and designing new catalysts, and 3DTI materials may offer rich opportunities for this purpose.

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