Supplementary Information

Selective CO_2 Reduction on Topological Chern Magnet $TbMn_6Sn_6$

Xi-Mei Li, Zheng-Zhe Lin*, Xin-Wei Chen and Xi Chen†

School of Physics, Xidian University, Xi'an 710071, China

* Corresponding Author. E-mail address: zzlin@xidian.edu.cn

† Corresponding Author. E-mail address: xichen_phys@xidian.edu.cn

1. Computing Hubbard *U* from linear response

A linear response approach[1] is employed to calculate the effective Hubbard *U*. The basic idea of this approach is the observation that the DFT total energy is a quadratic function of on-site occupations[2]. By the rotationally invariant formulation[3], the total energy functional of DFT + U can be written as

$$E_{\mathrm{DFT+U}}[n] = E_{\mathrm{DFT}}[n] + E_{\mathrm{U}}[n^{l\sigma}_{mm'}],$$

where E_{DFT} is a standard approximate DFT functional and E_{U} is the Hubbard correction, according to the simplified functional given by

$$E_{\mathrm{U}} = \sum_{l\sigma} \frac{U-J}{2} Tr[\boldsymbol{n}^{l\sigma}(1-\boldsymbol{n}^{l\sigma})] = \sum_{l\sigma} \frac{U_{eff}}{2} Tr[\boldsymbol{n}^{l\sigma}(1-\boldsymbol{n}^{l\sigma})].$$

By the linear-response *U* approach, the response function can be calculated as $\chi^{\mathbf{I}} = \partial n^{\mathbf{I}}/\partial \alpha^{\mathbf{I}}$, where $\alpha^{\mathbf{I}}$ represents the "strength" of the perturbation on atom **I** (usually chosen small enough to maintain a linear response regime) and $n^{\mathbf{I}}$ is the occupation. The interacting (χ) and the non-interacting (χ_0) density response functions of the system with respect to localized perturbations are first calculated. Then the Hubbard *U* can be obtained by $U_{eff} = 1/\chi - 1/\chi_0$.

VASP (version ≥ 5) can perform the linear response calculation with LDAU = T and LDAUTYPE = 3. In this case, LDAUU and LDAUJ should be both set as $\alpha^{\mathbf{I}}$, and $n^{\mathbf{I}}$ will be printed with LDAUPRINT = 2. The POSCAR of $TbMn_6Sn_6$ primitive cell reads (for the POSCAR file, see **Supplementary II**)

TbMn6Sn6

1.00000000000000

5.4465354000000001	**0.0000000000000000**	**0.0000000000000000**
-2.7232677000000001	**4.7168380000000001**	**0.0000000000000000**
0.0000000000000000	**0.0000000000000000**	**8.9694351999999995**

Tb Sn Mn

1 6 6

Direct

-0.0000000000000000	**0.0000000000000000**	**-0.0000000000000000**
0.3333333340000024	**0.6666666679999977**	**0.5000000000000000**
0.6666666109999966	**0.3333333089999968**	**0.5000000000000000**
0.3333333340000024	**0.6666666679999977**	**-0.0000000000000000**
0.6666666109999966	**0.3333333089999968**	**-0.0000000000000000**
-0.0000000000000000	**0.0000000000000000**	**0.6662294578627622**
-0.0000000000000000	**0.0000000000000000**	**0.3337705681372400**
0.5000000000000000	**0.0000000000000000**	**0.7515951515947960**
0.5000000000000000	**0.0000000000000000**	**0.2484048484052040**
0.0000000000000000	**0.5000000009999965**	**0.7515951515947960**
-0.0000000000000000	**0.5000000009999965**	**0.2484048484052040**
0.5000000000000000	**0.5000000009999965**	**0.7515951515947960**
0.5000000000000000	**0.5000000009999965**	**0.2484048484052040**

To calculate the linear response of one Tb atom in $TbMn_6Sn_6$, the parameters in the INCAR,are

LDAU = T ; LDAUTYPE = 3

LDAUL = 3 -1 -1

LDAUU = * 0 0**

LDAUJ = * 0 0**

LDAUPRINT = 2 ; LORBIT = 11

in which *** denotes the given $\alpha^{\mathbf{I}}$ for the Tb 4*f* orbital (in eV). The operation starts from a usual calculation with $\alpha^{\mathbf{I}} = 0$. With the generated CHGCAR and WAVECAR, the interacting (χ) density response calculation runs with given $\alpha^{\mathbf{I}}$ and ISTART = 1, ICHARG = 1. $n^{\mathbf{I}}$ can be found in the OUTCAR. For the non-interacting (χ_0) calculation

with given α^{I}, use ISTART = 1, ICHARG = 11 to keep the wavefunctions fixed. **Fig. S1** shows the results, in which n (n_0) is the occupation of interacting (non-interacting) calculation, respectively. By fitting the slopes, χ = 3.99 eV^{-1} and χ_0 = 0.30 eV^{-1}, and then $U_{eff} = 1/\chi - 1/\chi_0$ = 3.1 eV, are obtained.

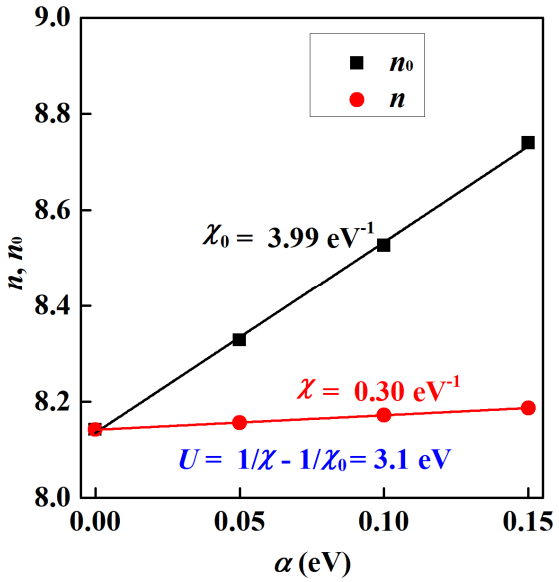

Fig. S1 The interacting (black) and non-interacting density response functions of Tb 4*f* orbital in $TbMn_6Sn_6$.

References:

[1] M. Cococcioni, S. de Gironcoli, *Phys. Rev. B* **71**, 035105 (2005).

[2] M. T. Czyżyk, G. A. Sawatzky, *Phys. Rev. B* **49**, 14211 (1994).

[3] S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys, A. P. Sutton, *Phys. Rev. B* **57**, 1505 (1998).

2. Atomic-orbital-resolved energy bands

Fig. S2 shows the energy bands of $TbMn_6Sn_6$ resolved by Tb and Mn atomic orbitals. The color shows the proportion of Tb / Mn atomic orbitals in the band states. We can see narrow Tb 4*f* bands near the Fermi level. Other bands near the Fermi level are mainly Mn 3*d* bands.

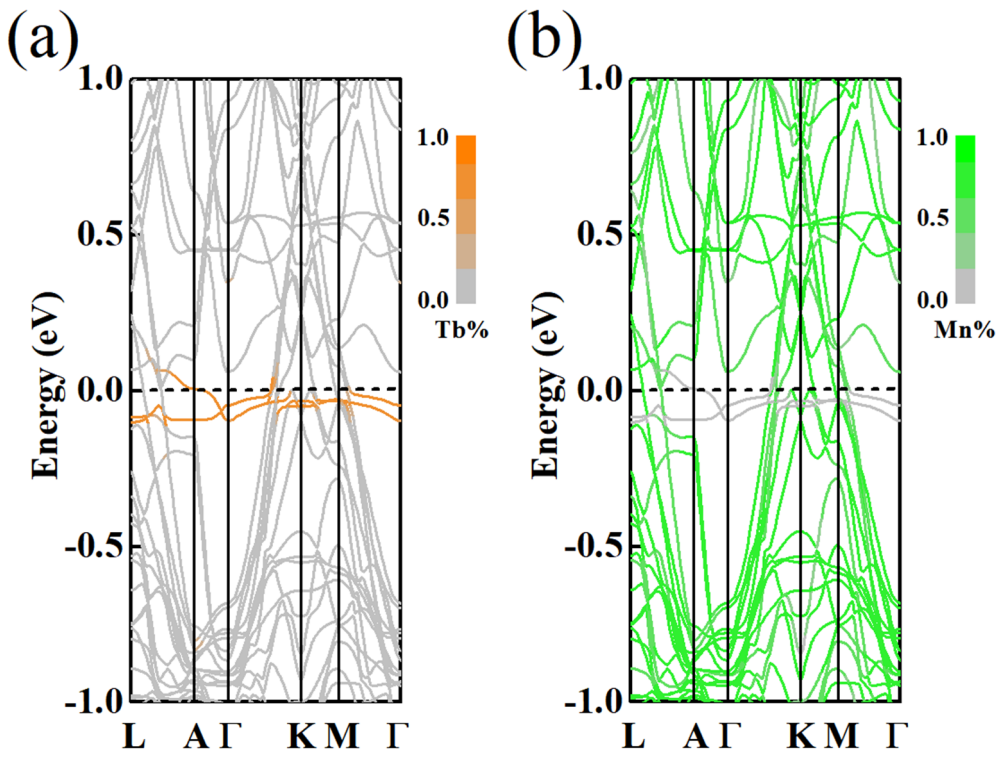

Fig. S2 The energy bands of $TbMn_6Sn_6$ resolved by Tb and Mn atomic orbitals. The Fermi level is set zero.

3. The Dirac points

To show the Dirac points generated by kagome Mn arrangement, the energy bands near the K point are enlarged in **Fig. S3**. We can see one Dirac cone below the Fermi level, and two Dirac cones above the Fermi level. Small gaps are opened by spin-orbit coupling.

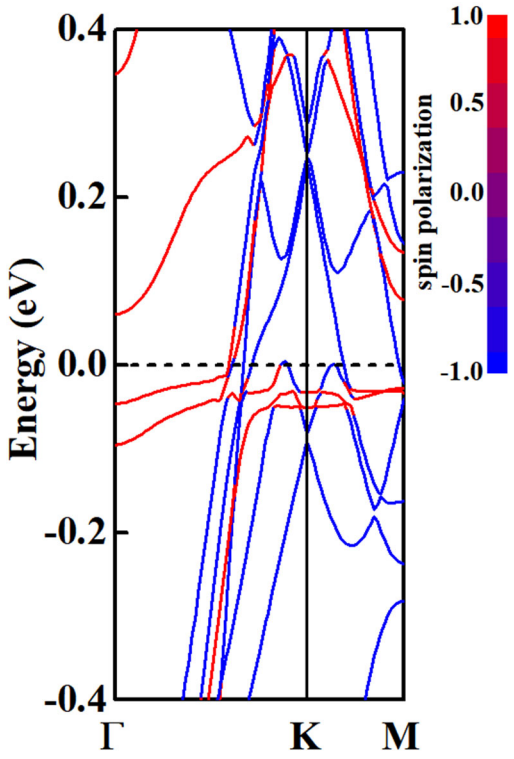

Fig. S3 The energy bands of $TbMn_6Sn_6$ near the K point. The spin-polarization of each state is resolved. The Fermi level is set zero.

4. Chemical potential of atomic layers in $TbMn_6Sn_6$

$TbMn_6Sn_6$ has a layered crystal structure, and its unit cell structure is ABCB stacking. In order to simplify the calculation, the chemical potential of each layer of $TbMn_6Sn_6$ is evaluated (instead of evaluating the chemical potential of each element), and only the interactions between the nearest and second-nearest layers are considered. Let's use I_{AB} represents the influence of layer B on the chemical potential of layer A. I_{BA}, I_{BC}, I_{CB}, I_{BB}, I_{AC} and I_{CA} have similar meaning. The chemical potentials of layers A, B, and C are

$$\begin{aligned} \mu_A &= \mu_{A0} + 2I_{AB} + 2I_{AC} \\ \mu_B &= \mu_{B0} + I_{BA} + I_{BC} + 2I_{BB} \\ \mu_C &= \mu_{C0} + 2I_{CB} + 2I_{AC} \end{aligned} \tag{S1}$$

Here, μ_{A0}, μ_{B0} and μ_{C0} represent the chemical potentials of the A, B and C layers without interactions, respectively. Suppose the symmetric relationships $I_{AB} = I_{BA}$, $I_{BC} = I_{CB}$, $I_{AC} = I_{CA}$. Under these assumptions, the free energy of $TbMn_6Sn_6$ unit cell reads

$$E_{cell} = \mu_{A0} + 2\mu_{B0} + \mu_{C0} + 4I_{AB} + 4I_{BC} + 4I_{AC} + 4I_{BB} \tag{S2}$$

The free energy of $TbMn_6Sn_6$ unit cell without one A layer reads

$$E_{(without\ A)} = 2\mu_{B0} + \mu_{C0} + 4I_{BC} + 4I_{BB} \tag{S3}$$

The free energy of $TbMn_6Sn_6$ unit cell without one B layer reads

$$E_{(without\ B)} = \mu_{A0} + \mu_{B0} + \mu_{C0} + 2I_{AB} + 2I_{BC} + 4I_{AC} \tag{S4}$$

The free energy of $TbMn_6Sn_6$ unit cell without one C layer reads

$$E_{(without\ C)} = \mu_{A0} + 2\mu_{B0} + 4I_{AB} + 4I_{BB} \tag{S5}$$

The free energy of $TbMn_6Sn_6$ unit cell without one A and one B layer reads

$$E_{(without\ AB)} = \mu_{B0} + \mu_{C0} + 2I_{BC} \tag{S6}$$

The free energy of $TbMn_6Sn_6$ unit cell without one B and one C layer reads

$$E_{(without\ BC)} = \mu_{A0} + \mu_{B0} + 2I_{AB} \tag{S7}$$

The free energy $TbMn_6Sn_6$ unit cell without one A and one C layer reads

$$E_{(without\ AC)} = 2\mu_{B0} + 4I_{BB} \tag{S8}$$

The relationships S2~S8 can be summarized as

$$\begin{pmatrix} E_{cell} \\ E_{(without\ A)} \\ E_{(without\ B)} \\ E_{(without\ C)} \\ E_{(without\ AB)} \\ E_{(without\ BC)} \\ E_{(without\ AC)} \end{pmatrix} = \begin{pmatrix} 1 & 2 & 1 & 4 & 4 & 4 & 4 \\ 0 & 2 & 1 & 0 & 4 & 0 & 4 \\ 1 & 1 & 1 & 2 & 2 & 4 & 0 \\ 1 & 2 & 0 & 4 & 0 & 0 & 4 \\ 0 & 1 & 1 & 0 & 2 & 0 & 0 \\ 1 & 1 & 0 & 2 & 0 & 0 & 0 \\ 0 & 2 & 0 & 0 & 0 & 0 & 4 \end{pmatrix} \begin{pmatrix} \mu_{A0} \\ \mu_{B0} \\ \mu_{C0} \\ I_{AB} \\ I_{BC} \\ I_{AC} \\ I_{BB} \end{pmatrix} \quad \text{(S9)}$$

DFT calculations are employed to calculate the above seven energy values on the left (E_{cell} = -89.94 eV, $E_{(without\ A)}$ = -63.01 eV, $E_{(without\ B)}$ = -55.20 eV, $E_{(without\ C)}$ = -77.19 eV, $E_{(without\ AB)}$ = -34.39 eV, $E_{(without\ BC)}$ = -43.49 eV, $E_{(without\ AC)}$ = -52.82 eV). Using the inverse of the matrix, μ_{A0}= -12.15 eV, μ_{B0}= -25.23 eV, μ_{C0}= -8.13 eV, I_{AB}= -3.06 eV, I_{BC}= -0.52 eV, I_{AC}= -0.64 eV, I_{BB}= -0.59 eV can be obtained. Finally, the chemical potentials μ_A= -19.54 eV, μ_B= -29.98 eV and μ_C= -10.44 eV of the A, B and C layers are calculated by Eq. (S1).

5 The structure of Sn bulk

Sn bulk has various phases including α-Sn, β-Sn, γ-Sn, simple hexagonal (sh), hexagonal close packed (hcp), body-centered tetragonal (bct), body-centered cubic (bcc), and face-centered cubic (fcc). At normal pressures, the three stable solid phases are α-Sn, β-Sn and γ-Sn (for the structures, see **Fig. S4(a)**, **(b)** and **(c)**), for which phase transition occurs at different temperatures. At low temperatures, the stable phase is α-Sn (diamond-like). At normal temperatures, the stable phase is β-Sn. At the temperatures close to the melting point (305 K), it changes to γ-Sn. We use γ-Sn to approximately represent the liquid phase. The POSCAR is listed below (for the POSCAR file, see **Supplementary II**).

Gamma-Sn
1.00000000000000
5.7463446548044628 0.0000000000000000 0.0000000000000000
0.0000000000000000 6.1331794691422576 0.0000000000000000
0.0000000000000000 0.0000000000000000 3.2280194327051928
Sn
4
Direct
-0.0000000000000000 0.0000000000000000 -0.0000000000000000
0.0000000000000000 0.5000000000000000 0.0000000000000000
0.5000000000000000 0.0000000000000000 0.5000000000000000
0.5000000000000000 0.5000000000000000 0.5000000000000000

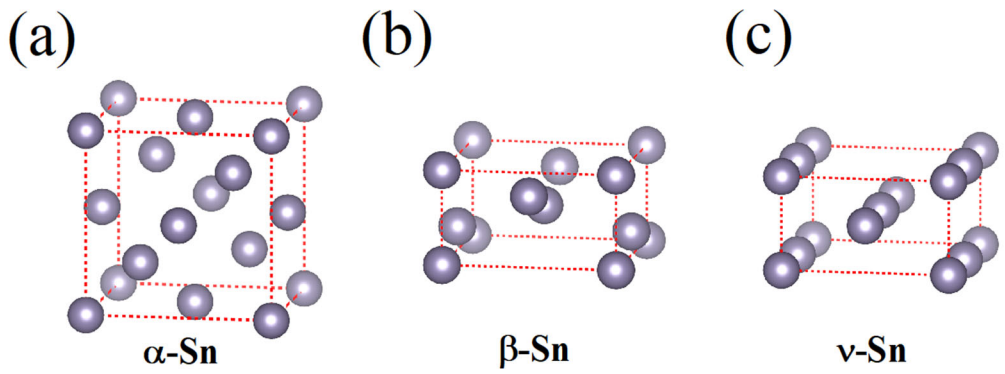

Fig. S4 The structures of **(a)** α-Sn, **(b)** β-Sn and **(c)** γ-Sn. The periodic boundary is shown by dashed liens.

References:

[1] B. H. Cheong and K. J. Chang, *Phys. Rev. B* **44**, 4103 (1991).

6 HER on the (001) surfaces of $TbMn_6Sn_6$

Fig. S5 shows the free energy profile of HER on the surfaces A, B1 and C of $TbMn_6Sn_6$. The computational hydrogen electrode model sets the free energies of H^+ + e and H_2 as zero. On the surfaces A, B1 and C, the onset potentials of HER are -0.79, -0.36 and -0.55 V, respectively.

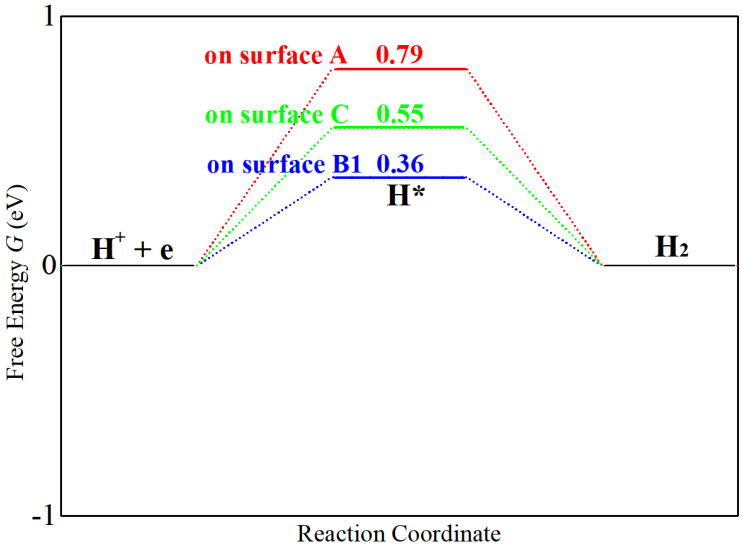

Fig. S5 The reaction free energy of hydrogen evolution reaction on the surfaces A, B1 and C of $TbMn_6Sn_6$.