

Supporting Information “Remarkably enhanced ferromagnetism in super-exchange governed Cr₂Ge₂Te₆ monolayer *via* molecular adsorption

Junjie He^{*,1,2}, Guangqian Ding², Chengyong Zhong^{1,2}, Shuo Li³, Dengfeng Li²,

Gang Zhang^{*,4}

¹*Institute for Advanced Study, Chengdu University, Chengdu 610100, P. R. China*

²*School of Science, Chongqing University of Posts and Telecommunications, Chongqing 400065, P. R. China.*

³*Faculty of Science, Charles University in Prague, Hlavova 8, 128 43 Prague 2, Czech Republic.*

⁴*Institute of High Performance Computing, A*STAR, Singapore 138632*

*E-mail: hejj@cqupt.edu.cn; zhangg@ihpc.a-star.edu.sg

1. Influence and origin of U-independent band structure of CGT

Generally, magnetic, electronic, and structural properties for transition-metal compounds are sensitive to local Coulomb interactions of d electron. The DFT+U approach has been widely used to investigate the transition-metal compounds because it can partially correct the artificially delocalized d orbital of TM atoms and inherent self-interaction errors for DFT. The local Coulomb interaction U value can enhance the exchange splitting of spin-up and spin-down of d states with metal-insulator transition as reported in transition-metal oxides.¹ For example, the DFT+U approach can reproduce the insulating ground states of NiO.

For CGT monolayer, by changing U value in the range of 0~3.5 eV (U=0 corresponding to the pristine GGA functional), we find that the band structures are sensitive to the choice of U value as shown in Figure S1. For example, when U = 0, the calculations show an insulating ground state with finite band gaps, while when U = 3.5 eV, it predicts a semi-metallic ground state for CGT, which contradicts the semiconducting behavior observed experimentally. Such results also coincide with the recent report.² We can conclude that the PBE with large U failure to describe the ground states properties of CGT system, while the PBE or PBE with small U approach can successfully describe the ground state properties. Therefore, instead of GGA+U, we use the GGA functional to study the molecule adsorption on CGT monolayer.

To understand the mechanism of U-induced anomalous “semiconductor-metal transition” in CGT sheet, the PDOS for Cr-d, Te-p and Ge-p orbital is presented in Figure S2, respectively. For U = 0, the valence band is mainly contributed by Te-p state in spin up channel, and while the conduction band is stem from the hybrid states of Cr-d, Te-p and Ge-p states, respectively. The occupied and unoccupied Cr d orbital in spin up channel is mainly localized in the range of [-3.6, -0.4] eV and [0.25, 2.2] eV, respectively. On the other

side, for spin down channel, the unoccupied Cr *d* orbital is localized above 0.12 eV, indicating the large exchange spin splitting between spin up and down of *d* orbital. The schematic energy diagram of the CGT electronic structure is present in Figure S3. The increase of *U* pushes down the localized spin up Cr *d* orbital, while the spin down spin down Cr-*d* together with hybridized Ge-*p* and Te-*p* state shift towards higher energy level. However, the top of valence band is dominated by the Te *p* component, which is not affected by the change of *U* parameter. Therefore, the increasing *U* contributes to the relative downward shift of the spin up Cr-*d* band, thereby leading to the semiconductor-metal transition.

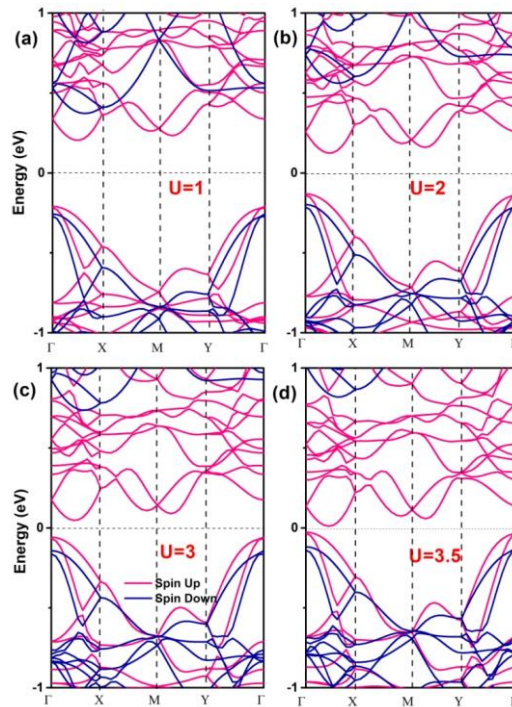


Figure S1. The band structures of CGT are presented in (a) $U=1$ eV, (b) $U=2$ eV, (c) $U=3$ eV and (d) $U=3.5$, respectively. The pink (blue) lines represent the spin-up (spin-down) bands. The Fermi level is set to zero.

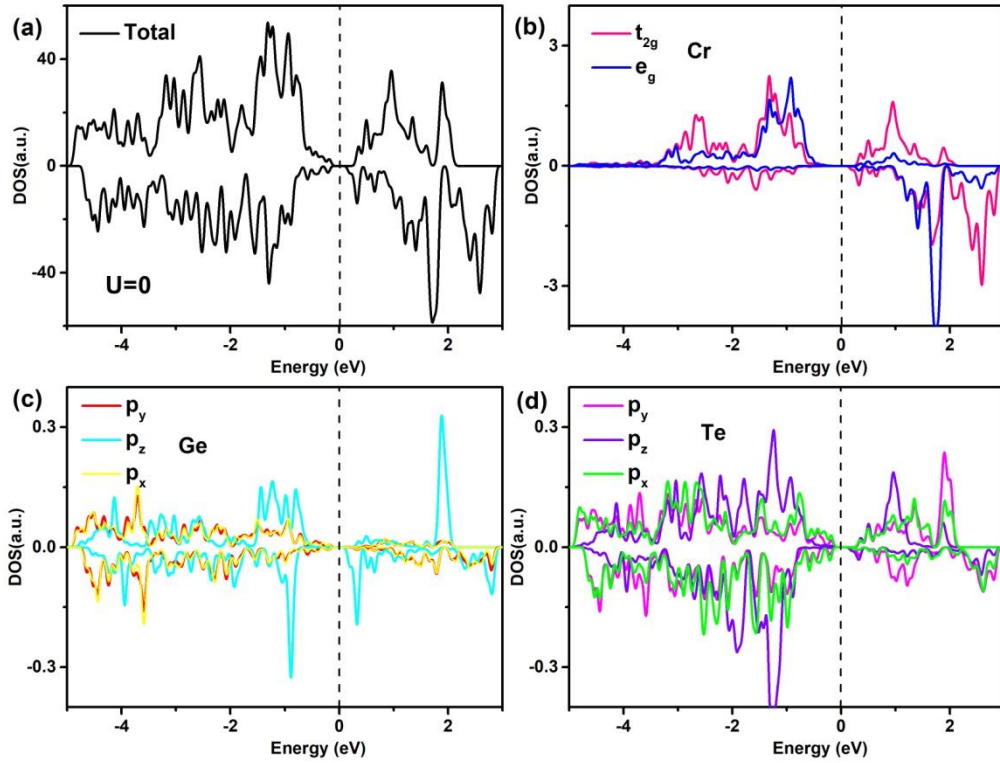


Figure S2. The total DOS (a) and PDOS of Cr (b), Ge (c) and Te (d) atoms for CGT in $U=0$ eV are shown, respectively. The Fermi level is set to zero.

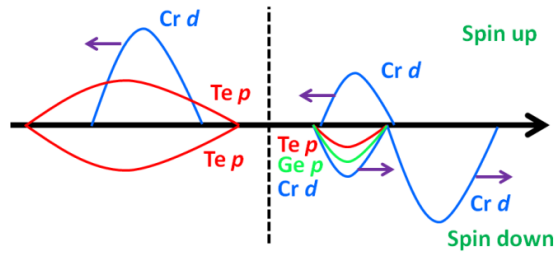


Figure S3: Schematic energy diagram of the CGT electronic structure. The primary features are the valence band and conduction band bands of (Te- p) and (Te-Ge-Cr) hybridized states, whereas the localized Cr d bands are split into the spin-up and spin-down channels with large exchange splitting. The Cr d band shifting with respect to the increasing U is shown by the violet arrow.

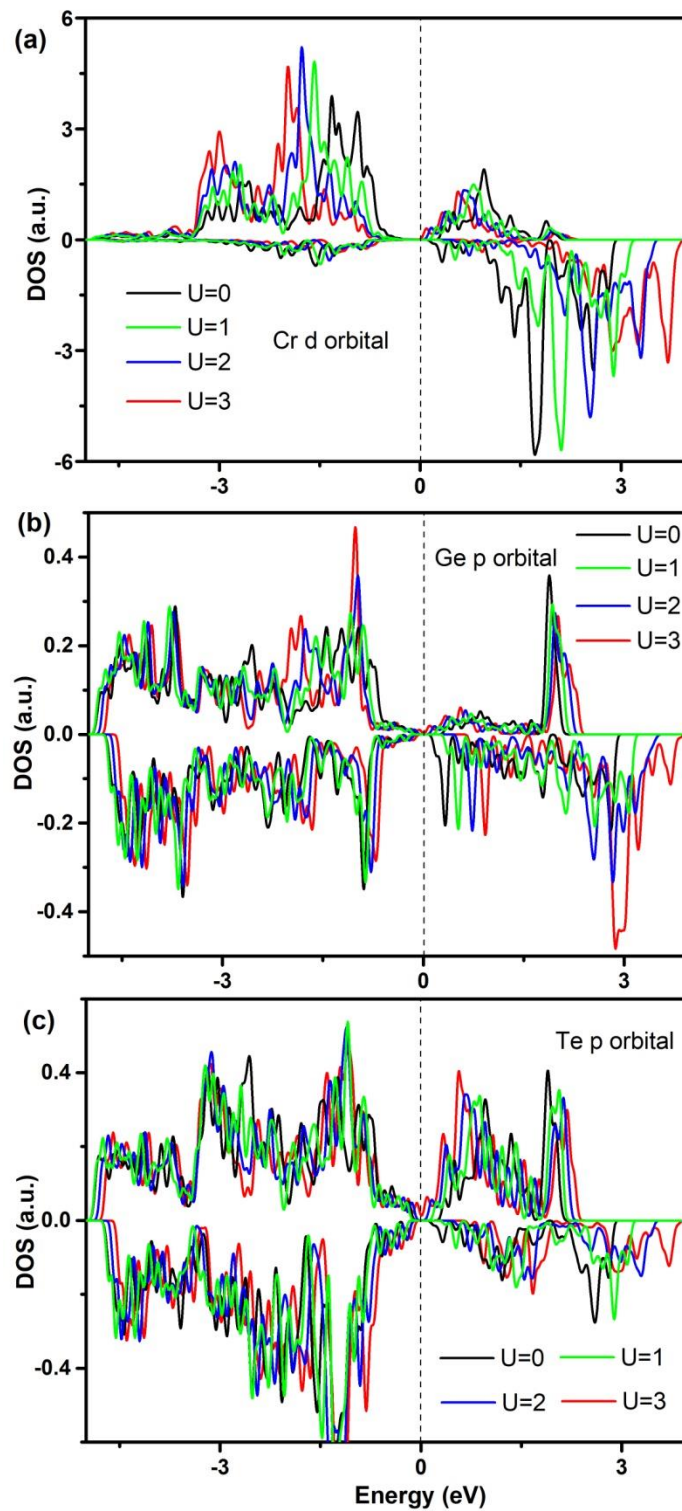


Figure S4. The PDOS of CGT for Cr-d (a), Ge-p (b), Te-p (c) orbital are presented in various U value.

2. Possible perpendicular adsorption configurations for molecule adsorbed on CGT

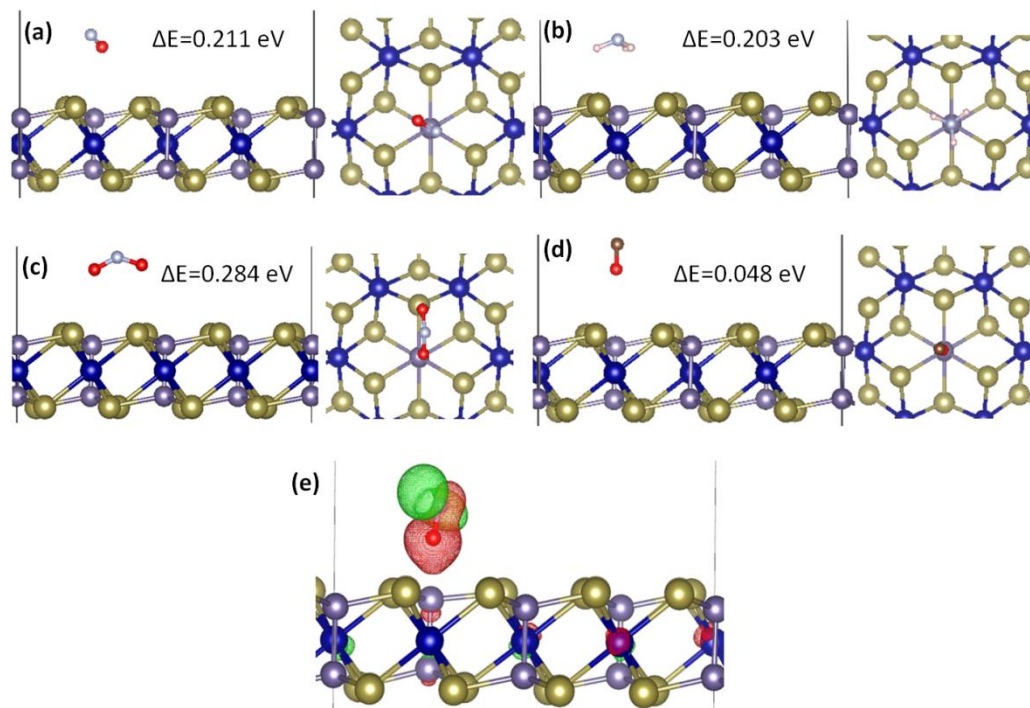


Figure S5. The O/H of (a) NO, (b) NO₂, (c) NH₃ and (d) CO towards the surface of CGT sheets. The energy difference (ΔE) between O/H and C/N towards the surface of CGT sheets are marked, respectively. The more positive value of ΔE represent the more high stability for the structure of C/N towards the surface of CGT sheets. (e) The differential charge density of NO adsorbed monolayer CGT sheet with isosurface value of $6 \times 10^{-4} \text{ e}/\text{\AA}^3$.

3. Band structure for CO, CO₂, H₂O, N₂ and SO₂ adsorbed CGT sheet.

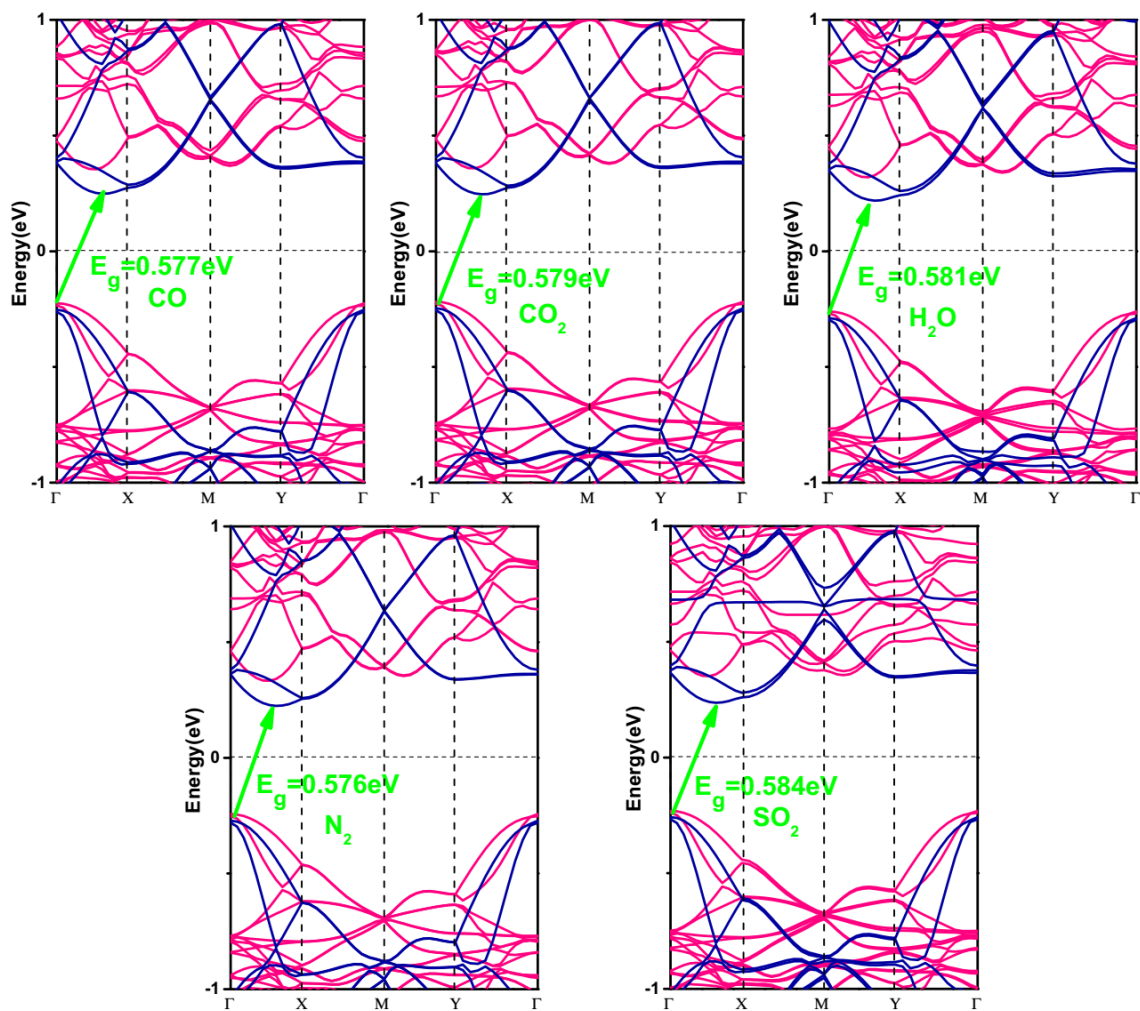


Figure S6. The band structures of CO, CO₂, H₂O, N₂ and SO₂ adsorbed CGT monolayer, respectively.

The pink (blue) lines represent the spin-up (spin-down) bands. The value of band gap for selected gas adsorption is labeled as well.

4. Band structure for NO₂ adsorbed CGT in various functional.

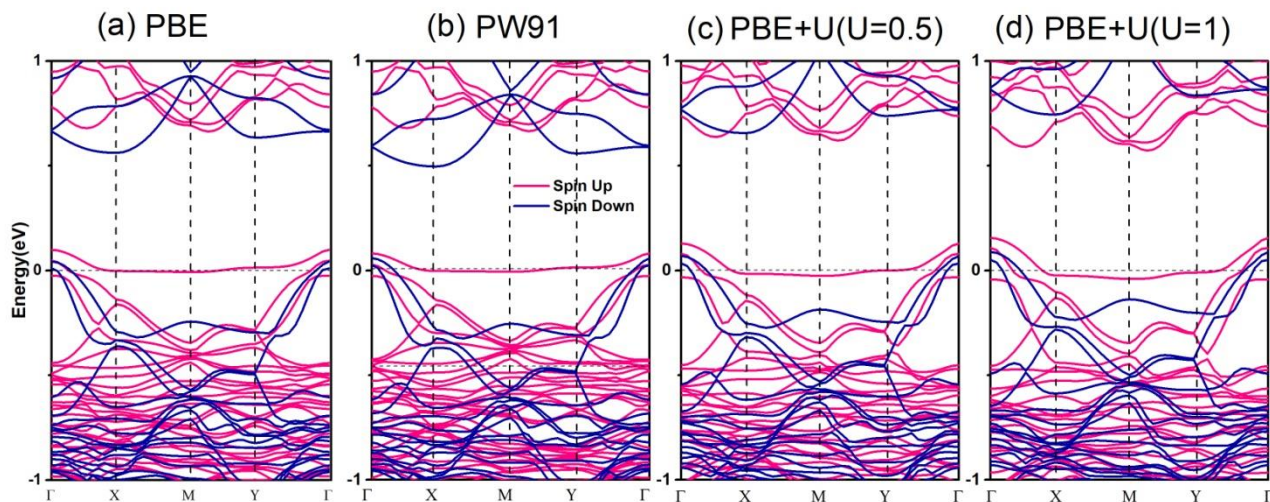


Figure S7. Band structure for NO₂ adsorbed CGT sheets in (a) PBE, (b) PW91, (c) PBE+U=0.5 eV and (d) PBE+U=1 eV functional.

5. The partial (total) density of states for molecule adsorbed CGT

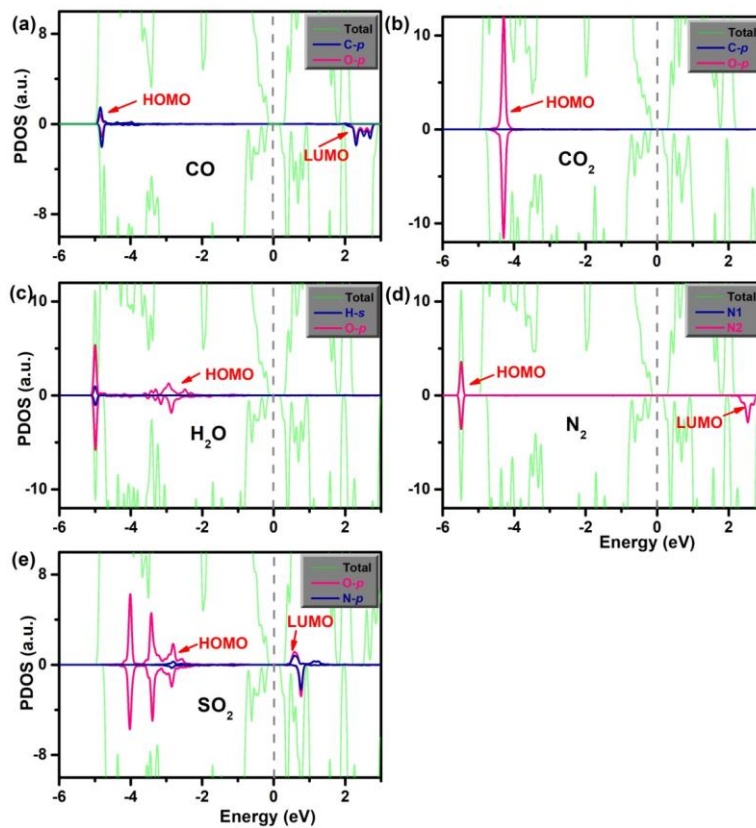


Figure S8. The partial (total) density of states of (a) CO, (b) CO₂, (c) H₂O, (d) N₂ and (e) SO₂ adsorbed CGT system. The Fermi level is set to zero.

6. The DOS for isolated molecule.

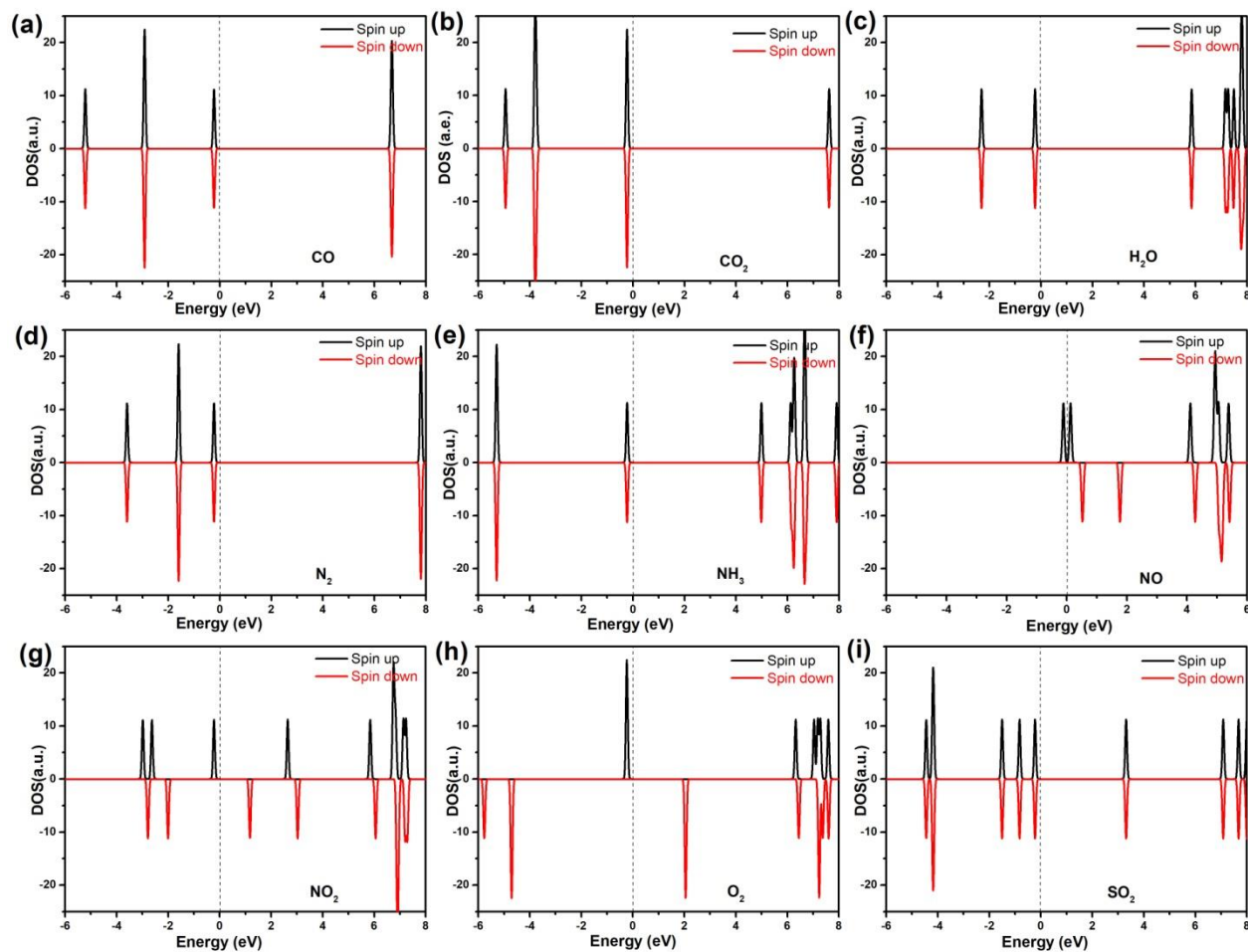


Figure S9. The DOS of isolated molecule for (a) CO, (b) CO₂, (c) H₂O, (d) N₂, (d) NH₃, (e) NO, (f) NO₂, (g) O₂ and (h) SO₂ are shown, respectively. The Fermi level is set to zero.

7. The structure and electronic properties for molecule distorted CGT sheet

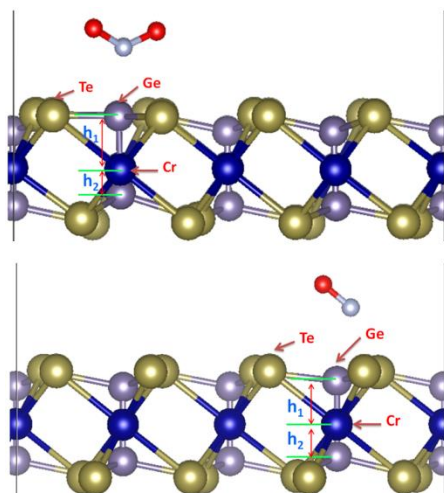


Figure S10. The relaxed structure for NO and NO₂ adsorbed CGT sheet. The vertical shifting distance (h_1 and h_2) for Ge-Ge dimer with respect to the Cr atoms position are marked, respectively.

Table S1: The h_1 and h_2 denote the vertical shifting distance for Ge-Ge dimer with respect to the Cr atoms position. The $h_{\text{Ge-Ge}}$ represents the distance of Ge-Ge dimer. The corresponding atomic structures are presented in Figure S9.

	NO	NO ₂	NH ₃	CGT
h_1	1.400	1.698	1.479	1.212
h_2	1.042	0.803	0.975	1.212
$h_{\text{Ge-Ge}}$	2.442	2.501	2.455	2.424

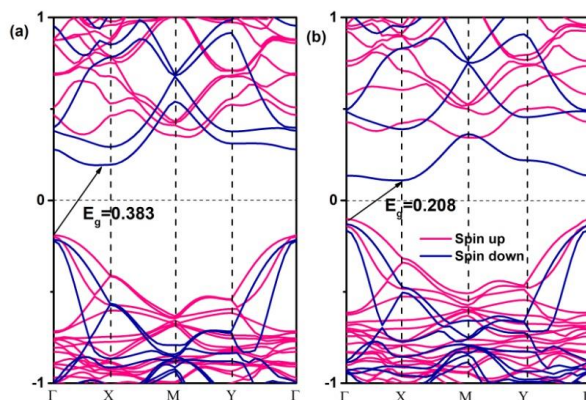


Figure S11. Band structure of distorted CGT induced by (a) NO and (b) NO₂ adsorption. The corresponding band gap are marked, respectively.

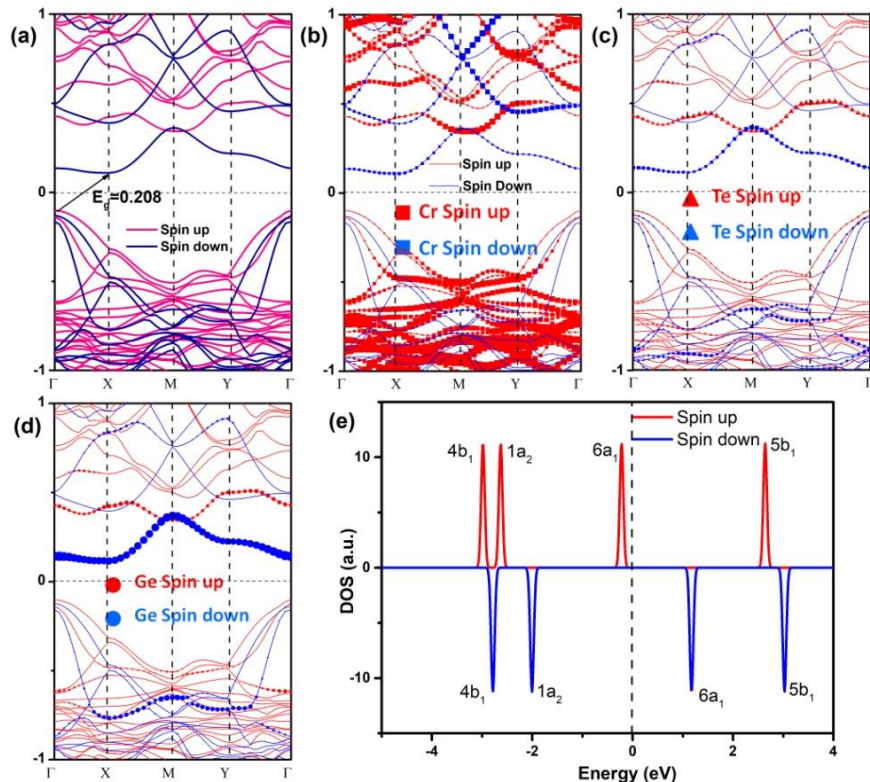


Figure S12. (a) Band structure of distorted CGT induced by (a) NO₂ adsorption, and (b) the corresponding band structures with the orbital weights for (b) Cr, (c) Te and (d) Ge atoms.

Square, triangle, and circle marks represent the weights of the Cr, Te, and Ge atoms, respectively. (d) the DOS for NO₂ molecule also shown. The Fermi level is set to zero.

8. Projected band structure for NO₂ adsorbed CGT.

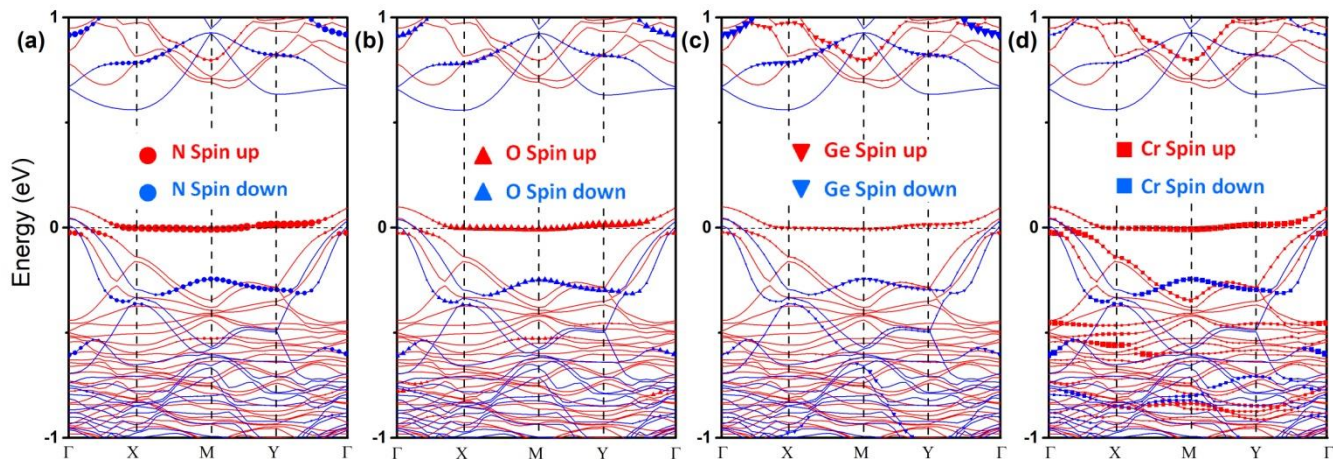


Figure S13. The band structures of NO₂ adsorbed CGT sheets with the orbital weights for (a) N, (b) O, (c) Ge and (d) Cr atoms, respectively.

Reference:

¹ O. Bengone, M. Alouani, P. Blöchl, J. Hugel, *Phys. Rev. B*, 2000, **62**(24), 16392.

² S. Kang, S. Kang, J. Yu, 2018. *Journal of Electronic Materials*, 2019, **48**, 1441–1445.