## 1 Supporting information

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- 3 Interfacial structure-governed SO<sub>2</sub> resistance of Cu/TiO<sub>2</sub> catalysts in the catalytic
- 4 oxidation of CO
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Fig. S1 CO oxidation activity over (a) fresh DT and its reduced counterparts under H<sub>2</sub> atmosphere at different temperatures; and over (b) different types of fresh Cu-Ti catalysts as well as their reduced ones as a function of temperature.

|          | Atomic fraction (%) |       |          |      |  |
|----------|---------------------|-------|----------|------|--|
| catalyst | Fresh               |       | Sulfated |      |  |
|          | Cu                  | Ti    | Cu       | S    |  |
| DT       | 2.13                | 35.58 | 1.20     | 0.75 |  |
| SFT      | 3.09                | 31.75 | 1.62     | 1.36 |  |
| MT       | 0.67                | 35.81 | 0.81     | 0.24 |  |

Table S1 EDS results of Cu, Ti and S over fresh and sulfated catalysts based on HADDF mapping.



**Fig. S2** TEM images of fresh (a) DT, (b) fresh SFT, (c) fresh MT, and (d) sulfated DT, (e) sulfated SFT, (f) sulfated MT. Inset graphs refer to the particle size distribution obtained by measuring 60-80 grains for each sample.



**Fig. S3** HADDF mapping of Cu, S and Ti over selected regions of (a) sulfated DT, (b) sulfated SFT and (c) sulfated MT.



Fig. S4 TGA patterns of sulfated catalysts (30-900°C;10°C/min).

Thermogravimetric analysis (TGA) was used to study surface species formed on the three sulfated catalysts (which have been exposed to SO<sub>2</sub> (50 ppm) at 250°C for 12h during the catalytic oxidation of CO process; the reaction conditions are same to those in Fig. 1b). As shown in Fig. S4, all the sulfated catalysts undergo similar decomposition with increasing temperature. The weight loss below 200°C can be due to evaporation of adsorbed water while that between 200 and 450°C may arise from weakly adsorbed  $SO_2$  or sulfite species on the surface.<sup>1</sup> When the temperature further increased, the weight loss comes from the decomposition of "H<sub>2</sub>SO<sub>4</sub> like" species (which linked weakly to Cu sites) and closely connected CuSO<sub>4</sub> species. For all the sulfated catalysts, the amount of sulfate species formed during  $SO_2$  exposure is small, hence the weight loss is not obvious, especially for MT. Assume that (1) Cu acts as active site to adsorb and transform  $SO_2$  into sulfate above  $370^{\circ}$ C; (2) each Cu site can transform one SO<sub>2</sub> molecule into one sulfate molecule; and (3) all sulfate species can decompose completely in the end of heating process. According to TGA curves, the weight loss caused by decomposition of sulfate (to gaseous  $SO_2$  or  $SO_3$ ) is 3.66 wt%, 2.54wt% and 0.6wt % for DT, SFT and MT, respectively. Since the resulting SO<sub>2</sub> (or SO<sub>3</sub>) has a similar relative molecular mass (ca. 64-80) to Cu (ca. 64), the weight loss rate is close to effectivelyaccessible Cu ratio, i.e., approximately 3.66 wt%, 2.54wt% and 0.6wt % for DT, SFT and MT, respectively. Because TGA experiments involve both surface and bulk processes. Combining the Cu loading on catalysts (Table 2), it can be speculated that the highly dispersed Cu species on DT enable almost complete access of Cu site to SO<sub>2</sub> while the aggregated Cu species on SFT and MT failed. However, due to limited accuracy of TGA data and other influencing factors (e.g. oxygen vacancies, reactive oxygen species, role of Ti, etc.), this speculation still needs more substantiated evidence.



Fig. S5 O<sub>2</sub>-TPD profiles of catalysts.

Temperature programmed desorption of  $O_2$  ( $O_2$ -TPD) experiments are carried out over catalysts on Chemisorb tp-5080 (Xianquan, Tianjin). Each sample (100 mg) was pretreated with high-purity Ar (50 mL/min) for 1h at 200°C and then cooled down to room temperature. The pretreated sample was exposed to 20% $O_2$ /Ar for 1h at room temperature, followed by purging with Ar till no change of baseline was observed. Then the sample was heated up to 700°C with a ramp rate of 10°C/min. The outflow gas was monitored by a thermal conductivity detector (TCD).

As shown in Fig. S4, for DT and SFT, the peaks centered at 163, 220 and 292°C are attributed to adsorbed molecular  $O_2$ ,  $O_2^-$  and  $O_2^{2-}$  on oxygen vacancies, respectively. <sup>2-4</sup> In addition, the peak at 466°C for DT can be due to the evolution of surface lattice oxygen. For MT, adsorbed molecular  $O_2$  needs a higher temperature (247°C) to be activated into  $O_2^-$  on oxygen vacancies, and then from  $O_2^-$  to  $O_2^{2-}$  at 335°C. The peak at 431°C is related to surface lattice oxygen. By comparison, DT possessed the largest amount of reactive oxygen species ( $O_2^-$  and  $O_2^{2-}$  at 220 and 292°C) among the three samples.



Fig. S6 Optimized adsorption models of SO<sub>4</sub><sup>2-</sup> and CO<sub>3</sub><sup>2-</sup> on TiO<sub>2</sub>, DT and SFT catalysts.



Fig. S7 Side and top view of DT catalyst and the enlarged Cu-O-Ti structure, in which the bader charges of the marked atoms are shown in Table S2.

| Charges / e      | Cu    | Oi    | O <sub>i</sub> ' | O <sub>ii</sub> | O <sub>ii</sub> ' | O <sub>iii</sub> | Ti <sub>i</sub> | Ti <sub>ii</sub> | Ti <sub>iii</sub> |
|------------------|-------|-------|------------------|-----------------|-------------------|------------------|-----------------|------------------|-------------------|
| $m_0 + \Delta m$ | 9.69  | 6.72  | 6.91             | 6.93            | 6.94              | 6.89             | 2.05            | 2.09             | 2.04              |
| Δm               | +1.31 | -0.72 | -0.91            | -0.93           | -0.94             | -0.89            | +1.95           | +1.91            | +1.96             |

 Table S2 Bader charge analysis of the excess electron.

The  $m_0$  represents the valence electron of the atom while  $\Delta m$  was charged electrons.



**Fig. S8** Possible positions for formation of O vacancies in TiO<sub>2</sub> and DT. The O vacancy (V<sub>0</sub>) formation energies have been listed in Table S3.

**Table S3** Optimized O vacancy ( $V_O$ ) formation energies (eV) in different positions (denoted as  $P_{i,}$ <sub>ii</sub>, ... or  $P_{i'}$ ,  $P_{ii'}$ ...) in TiO<sub>2</sub> and DT

|                  | Position          | $E_{f}(O \text{ rich}) / eV$                | $E_{f}$ (O poor)/eV       |  |
|------------------|-------------------|---|---------------------------|--|
|                  | O atom            | (in molecular O <sub>2</sub> )<br>-4.390132 | (Lattice O)<br>-11.098907 |  |
| TiO <sub>2</sub> | P <sub>ii</sub>   | 5.797888                                    | -0.910887                 |  |
|                  | P <sub>i</sub> ,  | 5.347518                                    | -1.361257                 |  |
|                  | P <sub>ii</sub> , | 5.797838                                    | -0.910937                 |  |
|                  | P <sub>iii</sub>  | 5.497938                                    | -1.210837                 |  |
| DT               | P <sub>i</sub> ,  | 1.914868                                    | -4.793907                 |  |
|                  | P <sub>ii</sub> , | 1.487098                                    | -5.221677                 |  |
|                  | P <sub>iii</sub>  | 0.830588                                    | -5.878187                 |  |

The red-marked results are the most favorable  $V_0$  formation energies in TiO<sub>2</sub> and DT, which are used to depict the  $V_0$  formation energy-dependent oxygen chemical potential picture, as shown in Fig. 7e in the main text.

## Notes and references

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