Electronic Supplementary Information for

Synergetic Effects of Strain Engineering and Substrate Defect on Generating Highly Efficient Single-Atom Catalysts for CO oxidation[†]

Ke Zhao,^a Yandi Zhu,^a Jinlei Shi,^b Xingju Zhao,^b Rui Pang,^a Xinlian Xue,^a Xiaoyan Ren,^{*a} Xiangmei Duan,^c Z. X. Guo,^d and Shunfang Li^{*a}

^aSchool of Physics and Engineering, Zhengzhou University, Zhengzhou, Henan 450001. China.

^bBeijing Computational Science Research Center, Beijing 100193, China

^cDepartment of Physics, Faculty of Science, Ningbo University, Ningbo 315211,

China.

^dDepartments of Chemistry and Mechanical Engineering, and Zhejiang Institute of Research and Innovation, The University of Hong Kong, Hong Kong SAR

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- S1: Electronic energy levels obtained by spin-polarized calculations for the PdAu, Pd₂, and Au₂ dimers.



Fig. S1: (*Color online*) Electronic energy levels of the PdAu, Pd₂, and Au₂ dimers. (*a*) *PdAu*, (*b*) *Pd₂ and* (*c*) *Au₂*. *Fermi levels have been shifted to be zero*.

S2: Optimized structures and the binding energies (E_b) of a NM (NM= Pd, Au) monomer deposited on the single-layer WTe₂ substrate.



Fig. S2 (Color online) Optimized structures and binding energies (E_b) of a NM monomer (NM=Pd, Au) adsorbed on the representative high symmetry sites of P-WTe₂ substrate, as denoted by NM/P-WTe₂. (a) NM=Pd (b) NM=Au. Both top views and side views of most stable low energy structures are illustrated. Purple, blue, green and yellow spheres represent the Te, W, Pd and Au atoms, respectively.

S3: Formation energy (E_f) of defects as a function of strain energies.



Fig. S3 Here, the strain energy is defined by the energy difference $E_{strain} - E_{equil}$, where the E_{strain} and E_{equil} represent the energies of the defected WTe_2 substrate under applied compressive (tensile) strain and that of the equilibrium state, respectively.

S4: Optimized structures of a NM (NM= Pd, Au) monomer deposited on the defected WTe₂ substrate.



Fig. S4 (Color online) Optimized structures of a NM monomer adsorption on the surface Te vacancy $(V(T_D))$ site of WTe_2 substrate, as termed $NM@D-WTe_2$.(a) NM=Pd; (b) NM=Au.

As shown in **Fig. S4(a) and (b)**, the optimized Pd and Au single atom prefers to locate at the $V(T_D)$ site on the D-WTe₂ surface. In the optimized structures, the average Pd-W and Au-W bond length are 2.73 and 2.76 Å, respectively.

Note that if we manually push the Pd or Au atom visibly away from the $V(T_D)$ site, the Pd or Au monomer can be automatically relaxed back to the $V(T_D)$ site.

S5: DOS of the P-WTe₂ and D-WTe₂



Fig. S5 (Color online) DOS of WTe₂: (a) P-WTe₂ (b) D-WTe₂.

S6: Optimized geometric configurations of the $Pd_nAu_m@D-WTe_2$ complexes $(n+m \leq 2)$.



Fig. S6 (Color online) Local geometric configurations of the optimized $NM_2@D-WTe_2$ complexes: (a) $Au_2@D-WTe_2$; (b) $Pd_2@D-WTe_2$; (c) $PdAu@D-WTe_2$. Both top views (top panels) and sides views (bottom panels) are presented.

S7: Local projected DOS of Pd--Au and Au--Au on the D-WTe₂ substrate.



Fig. S7 (Color online) Local projected DOS of the Pd and Au atoms in (a) Pd--Au@D- WTe_2 with $\varepsilon = 0\%$; (b) Au--Au@D- WTe_2 with $\varepsilon = +2\%$. In Pd--Au@D- WTe_2 , the Au atom is located on the $V(T_D)$ site and the Pd monomer is stabilized on the H1 site. In Au-Au@D- WTe_2 , one Au is trapped in the $V(T_D)$ site, the other Au is located on the T1 site, as termed Au_V and Au_{T1}, respectively.

S8: CO oxidation on Pd monomer site of Pd--Au@D-WTe₂ via the L-H mechanism.



Fig. S8 (Color online) Minimum energy path (MEP) of the CO oxidation on the Pd monomer site of Pd--Au@D-WTe₂ complex via the L–H mechanism. (I) the first CO

molecule oxidation. (II) MEP of the second CO oxidation based on the optimized structure of CO_2 emission in FS of (I). The initial, transition, and final states are denoted as IS, TS, and FS states, respectively. (III) The values of the TS1, TS2 and TS3 as a function of loaded strain ε are inserted.

Here, we note that, similar to the cases in the E–R process, the values of E_a in the ratelimiting step are further lowered in consideration of ZPE correction. However, the reduction of the E_a in L-H process is almost negligible, i.e., 12 meV for ϵ =-2% and 2 meV for -5%, respectively.

S9: CO oxidation on Au_{T1} monomer site of Au--Au@D-WTe₂ via the L-H mechanism with ϵ =+2%.



Fig. S9 (Color online) Catalytic circle of CO oxidation on the Au active site in Au-Au@D-WTe₂ system under $\varepsilon = +2\%$. The transition states (TS) are marked in the ratelimiting steps.

Our extensive calculations show that the CO oxidation prefers to proceed via the L – H mechanism on Au--Au@D-WTe₂. Namely, on Au--Au@D-WTe₂ [see Fig. S9 (i)], the incoming CO molecule first co-adsorbs with O₂ on the single Au atom and consequently a carbonate (CO₃) species is produced [see Fig. S9(ii)]. After overcoming relatively smaller $E_a = 0.16$ eV [see Fig. S9(iii)], consequently one linear CO₂ molecule is

produced [see Fig. S9(iv)] with an exothermic energy of 1.60 eV, as detailed by the minimum energy path (MEP) and energetics shown in Fig. S9. After that, one O atom is still left from the dissociated O₂ molecule [see Fig. S9(v)]. The second incoming CO molecule directly attacks the left O atom and consequently produces one linear CO₂ molecule with an exothermic energy of 3.47 eV. In this process, the CO is first weakly adsorbed around the previously left O with a distance of 3.13 Å [see Fig. S9(vi)], upon overcoming a small E_a of 0.19 eV, a CO₂ molecule can be readily emitted [see Fig. S9(vii)]. The transition state is denoted as TS2 in [Fig. S9(vii)], wherein the CO molecule is about 2.27 Å away from the O atom. Then, a catalytic cycle of CO oxidation on Au--Au@D-WTe₂ is finished. Upon that, we have also further considered the ZPE corrections in calculation of the activation energy barrier (E_a) in the rate-limiting steps. The calculations show that the calculated E_a of the transition states of TS1 (TS2) in consideration of ZPE have been changed from 0.16 (0.19) to 0.15 (0.18) eV, as shown in Fig. S9†.

S10: Average cohesive energy ACE (or average binding energy) per atom of the optimized Au_N clusters and Au bulk.



Fig. S10 Average cohesive energy ACE (or average binding energy) per atom of optimized Au_N clusters and Au bulk. For comparison, the E_b (2.12 eV) of Au-SAC on P-WTe₂ is also highlighted by the red line as a reference.

Table S1: Comparison of calculated lattice constants of bulk WTe_2 in consideration of three representative van der Waals correction schemes with experimental values. Here, vdW (I), vdW (II) and vdW (III) denote zero damping DFT-D3 method of Grimme, DFT-D2 method of Grimme, and DFT-D3 method with Becke-Jonson damping, respectively. In the bracket, the calculation errors of the lattice constants (LC) with respect to experimental values are presented in the form of (LC(Calculation) –

LC(Experiment))/LC(Experiment) ×100%.

	а	b	с
experimental values	3.477	6.249	14.018
vdW (I)	3.484 (0.20%)	6.261 (0.18%)	14.046 (0.20%)
vdW (II)	3.487 (0.29%)	6.268 (0.30%)	14.060 (0.30%)
vdW (III)	3.460 (-0.49%)	6.218 (-0.50%)	13.948 (-0.50%)
without vdW	3.533 (1.61%)	6.349 (1.60%)	14.242 (1.60%)