Electronic Supplementary Information for

Synergetic Role of Charge Transfer and Strain Engineering in Improving the Catalysis of Pd Single-Atomic-thick motifs Stabilized on Defect-free MoS₂/Ag(Au)(111) Heterostructure

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Fig. S6 Schematic show TER mechanism of the CO oxidation on Pd_1/substrates.

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Table S1 Calculated work function (WF in eV) of the typical systems.

	MoS$_2$	Au(111)	Ag(111)	MoS$_2$/ Au(111)	MoS$_2$/ Ag(111)	Pd$_1$/MoS$_2$/ Au(111)	Pd$_1$/MoS$_2$/ Ag(111)
WF	5.68	5.18	4.61	5.36	4.76	4.96	4.67
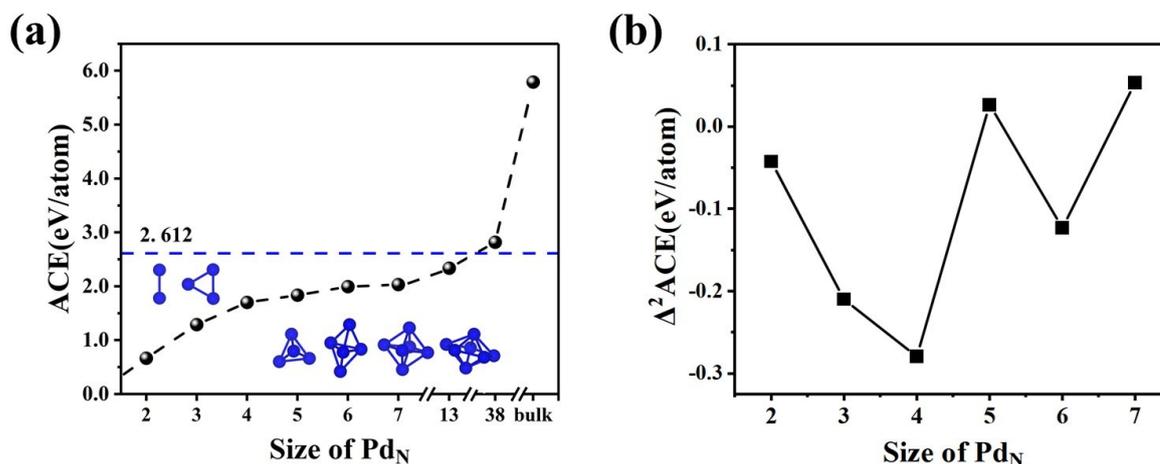
Fig. S1 (a) Geometric structures and average cohesive energies (ACE) of the most stable structures of Pd$_N$ clusters (N = 2-7) in gas phase. (b) The second order difference of the ACE presented in (a).

Fig. S2 Average adsorption energy (E$_a$) of the most stable structural configurations of 3D-Pd$_N$ species (N=4-7) with different configurations and adsorption sites.

Fig. S3 Average adsorption energy (E_a) of the most stable structural configurations of 2D-Pd$_N$ species (N=3-7) with different configurations and adsorption sites.

MoS$_2$ (0.802eV)
MoS$_2$/5.18% (0.889eV)
MoS$_2$/Au(111) (0.873eV)
MoS$_2$/Ag(111) (0.872eV)
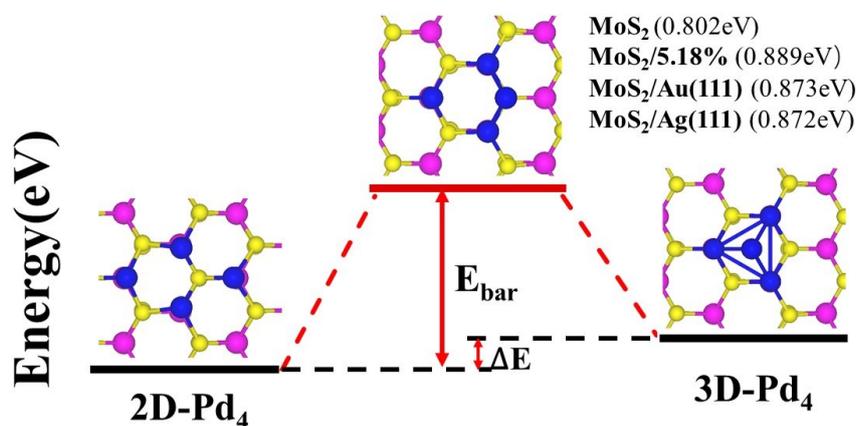
Fig. S4 Energy barrier (E_{bar}) for the phase transition from the 2D to 3D configurations.

we have demonstrated that, it is 2D-Pd$_3$ (rather than 2D-Pd$_4$) which displays significantly magic properties in the stability. Therefore, in experiment, 2D-Pd$_3$

possesses much longer life time than that of both 2D(3D)-Pd_4 and Pd_5. Moreover, as seen from **Fig. S4** even for the less stable species Pd_4, the calculated energy barrier (E_{bar}) for the phase transition from the 2D to 3D configurations is $E_{bar}= 0.872$ eV, which is significantly higher than the CO oxidation reaction barrier of 0.410 eV. According to the Arrhenius form of $R=R_0 \times exp[-E_{bar}/(k_B T)]$, with a typical prefactor of $R_0=10^{12}$/s, yielding a 2D to 3D phase transition rate of 2.253×10^{-3}/s at T~300K; nevertheless, the calculated $E_{bar}=0.763$ eV leads to a reaction rate of 1.526×10^{-1}/s at T~300 K for the phase transition from the 3D to 2D, which is about two orders of magnitude larger than that of the reversed process. These data suggest that, even though some 3D-Pd_N cluster may coexist with the 2D-Pd_N configurations, the 2D-Pd_N motifs should be dominant in experimental observations.

Table S2 Calculated O-O bond lengths, O_2-CO distances (d in Å) in the key steps shown in **Fig. 5(a)** for CO oxidations via TER mechanism on Pd_3/MoS_2, Pd_3/MoS_2/5.18%, Pd_3/MoS_2/Au(111), and Pd_3/MoS_2/Ag(111).

d(Å)	CO-O_2 (IS)	O-O (IS)	CO-O_2 (TS1)	O-O (TS1)	CO-O_2 (PS)	O-O (PS)	O-O (TS2)
MoS_2	3.325	1.273	1.843	1.315	1.336	1.434	1.434
MoS_2/5.18%	3.251	1.277	1.748	1.332	1.328	1.440	1.772
MoS_2/Au(111)	3.321	1.275	1.746	1.330	1.329	1.440	1.774
MoS_2/Ag(111)	3.255	1.283	1.696	1.347	1.357	1.437	1.762

Table S3 Adsorption energies (E_a in eV) of one CO, O_2, two CO (2CO), and O_2 and CO (O_2+CO) on only one Pd active site.

E_a(eV)	CO	O_2	2CO	O_2+CO
MoS_2	1.372	0.586	2.588	1.667
MoS_2/5.18%	1.106	0.562	2.290	1.385
MoS_2/Au(111)	1.107	0.568	2.324	1.135
MoS_2/Ag(111)	1.115	0.651	2.320	1.135
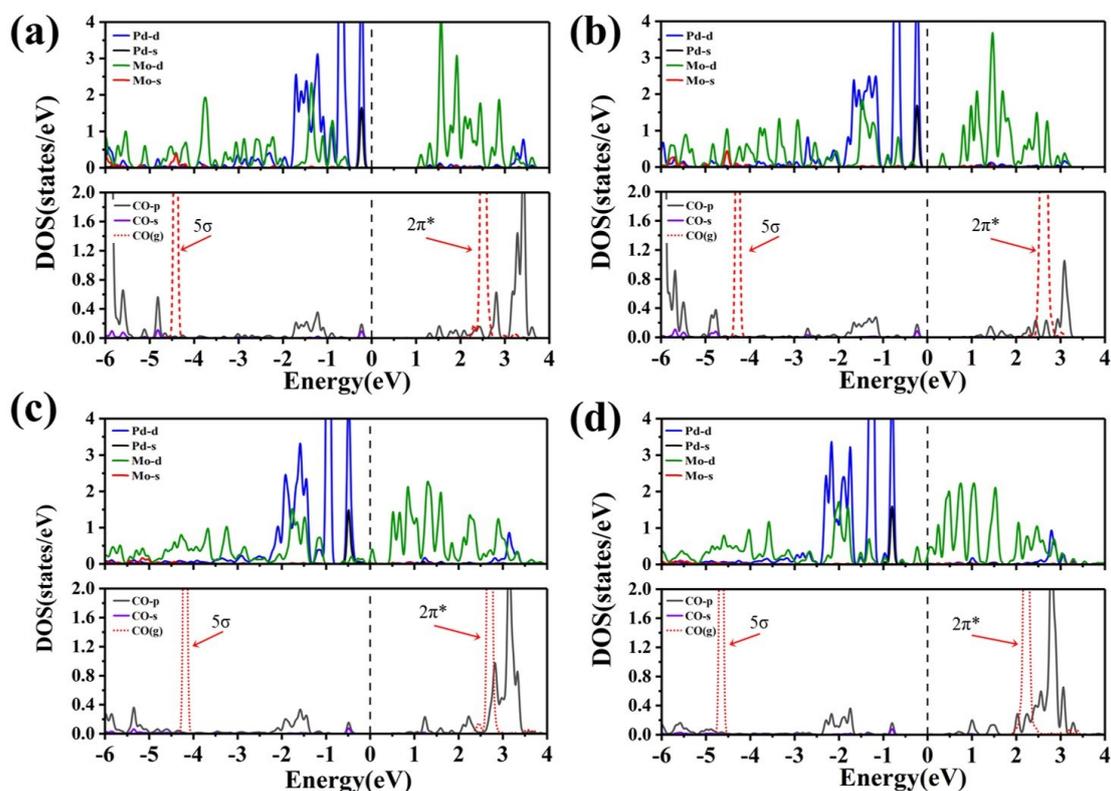
Fig. S5 Electronic density of states (DOS) of CO adsorbed on (a) Pd_1/MoS_2, (b) Pd_1/MoS_2/5.18%, (c) Pd_1/MoS_2/Au(111), and (d) Pd_1/MoS_2/Ag(111). For comparison, the DOS of gas phase CO far (more than 5 Å) above the Pd_1/substrates are also presented in red and dashed lines, with the Fermi levels shifted to zero.
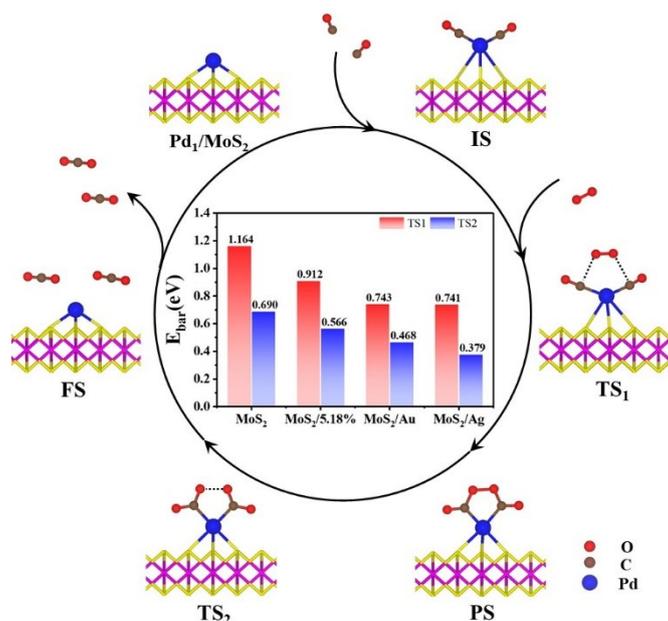
Fig. S6 Schematic show of the CO oxidation on Pd$_1$/substrates. TER mechanism, with the E$_{bar}$ obtained in TS$_1$ and TS$_2$.
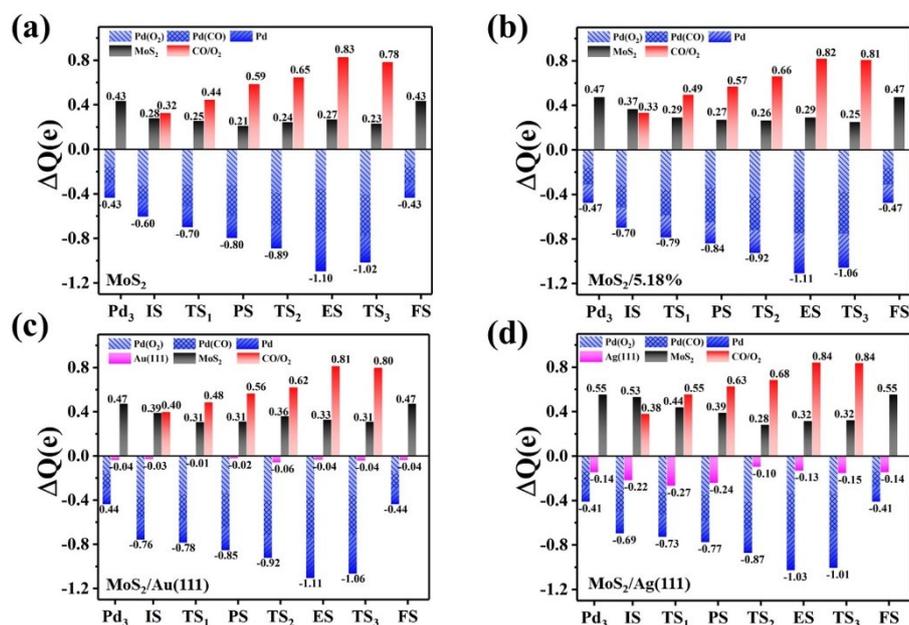
Fig. S7 Charge transfer (ΔQ) analysis of the CO oxidation (CLH) processes on 2D-Pd$_3$ species deposited on MoS$_2$, MoS$_2$/5.18%, MoS$_2$/Au(111), and MoS$_2$/Ag(111) substrates. Here, the three Pd atoms in 2D-Pd$_3$ magic motifs are tabbed as Pd(O$_2$), Pd(CO), and Pd, on which O$_2$, CO, and no molecule is adsorbed, respectively.