Supplementary Information for

Substrate Co-Doping Modulates Electronic Metal-Support Interactions and Significantly Enhances Single-Atom Catalysis

J. L. Shi,[a] J. H. Wu,[b] X. J. Zhao,[a] X. L. Xue,[a] Y. F. Gao,[c,d] Z. X. Guo,[e,a*] and S. F. Li[*a]

[a]*International Laboratory for Quantum Functional Materials of Henan, School of Physics and Engineering, Zhengzhou University, Zhengzhou, Henan 450001, China*

[b]*Department of Physics, Henan Institute of Education, Zhengzhou, 450046, China*

[c]*Department of Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee 37996, USA*

[d]*Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA*

[e]*Department of Chemistry, University College London, London WC1H 0AJ, UK*

This file includes:

S1: Details on the simulation methods

The electronic wave functions were expanded in a plane wave basis with an energy cutoff of 500 eV. To obtain the correct band gap of the TiO_2, we used the DFT+U method with U=5.5 eV (Note： our tests show that the choice of U values around 5.0 eV lead to negligible differences for the calculated results, such as the adsorption energy O_2 molecule and reaction barrier for CO oxidation). The calculated lattice parameters for primitive rutile TiO_2 unit cell are a = b = 4.662 Å and c = 2.959 Å, respectively, in good agreement with experimental result.[1] The rutile TiO_2(110) surface was simulated by a periodic four-layer *c*(4×2) slab model consisting of 192 atoms with ~13 Å of vacuum in between the slabs. The k-space integration was carried out using a Monkhorst-Pack grid of 2×3×1 **k** points in the surface Brillouin zone of the *c*(4×2) unit cell. All atoms except those in the bottom layer were allowed to relax along the calculated forces until all the residual force components were less than 0.01 eV/Å. In consideration of the experimental condition and previous calculations, we performed calculations that the Pd ad-atom is located in the vicinity of surface oxygen vacancy (V_O) site of the rutile rutile TiO_2 (110) which is denoted as Pd@TiO_2(110) throughout the document. For the interaction of the O_2 (CO) molecule with the Pd@TiO_2(110) catalyst, we initially placed the O_2 (CO) molecule about 4.5 Å away from the Pd atom followed by fully structural optimization. Bader charge analysis[2] is applied to evaluate the charge transfer.

S2: The optimized geometric structures of Pd@TiO_2(110) and the minimum energy path for CO oxidation on it.

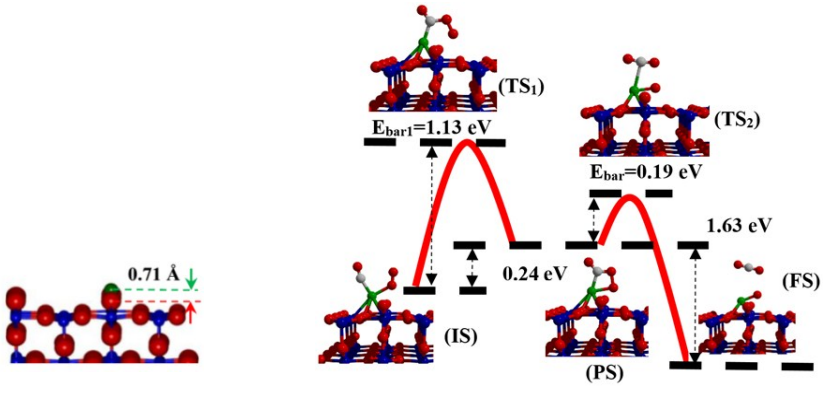

Fig. S1 (color online) **(A)** The optimized geometric structures of Pd@TiO_2(110); **(B)** the minimum energy path for CO oxidation on Pd@TiO_2(110). Note that though the Pd atom

prefers to locate in the oxygen vacancy site as presented in **(A)**, upon O_2 and CO adsorption, the deposited Pd atom migrates slightly from the vacancy site, as shown in **(B)**.

S3: Average bond lengths of the Pd atom with the surface Ti and O atoms of the co-doped substrates before and after O_2 adsorption.

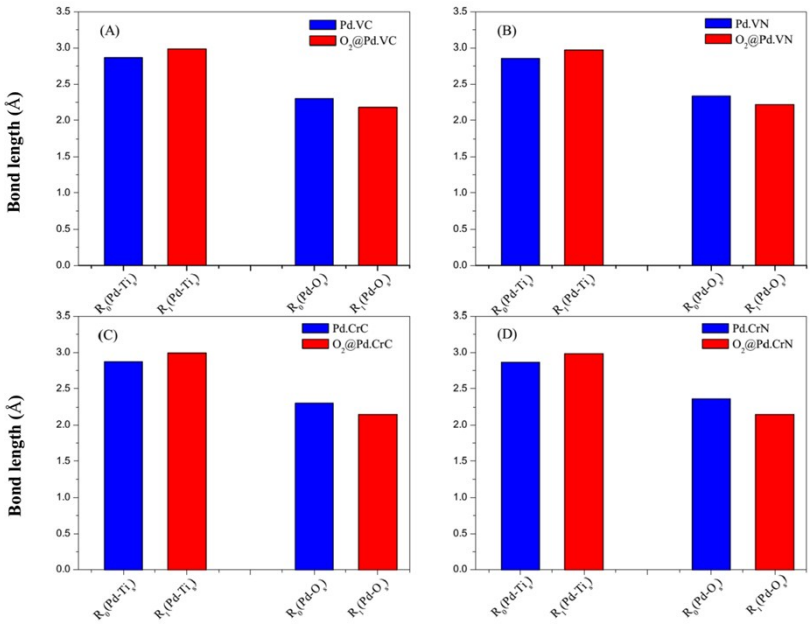

Fig. S2. Bond lengths of Pd atom with the Pd@TiO_2(110) and O_2-Pd@TiO_2(110) complexes with **(A)** V-C; **(B)** V-N; **(C)** Cr-C; and **(D)** Cr-N co-dopant pairs.

In Fig. S2, we provide average bond lengths of the Pd atom with the surface Ti and O atoms of the co-doped substrates, R_i(Pd-Ti_s) and R_i(Pd-O_s); i=0 and 1 correspond to the cases before and after O_2 adsorption on the supported Pd atom, respectively. One can readily see that the values of R_1(Pd-Ti_s) are increased after O_2 adsorption, however, the values for R_1(Pd-O_s) are decreased, indicating an weakened Pd-Ti_s interaction and enhanced Pd-O_s binding. To clearly illustrate the bond length changes, we summarize the calculated R_i(Pd-Ti_s) and R_i(Pd-O_s) in the table as follows:

Co-doped systems	R_i(Pd-Ti_s) **(Å)**	R_i(Pd-O_s) **(Å)**
Pd@TiO_2:V-C	r2.869	2.299
O_2-Pd@TiO_2:V-C	2.989	2.182
Pd@TiO_2:V-N	2.858	2.337
O_2-Pd@TiO_2:V-N	2.975	2.218
Pd@TiO_2:Cr-C	2.872	2.302
O_2-Pd@TiO_2:Cr-C	2.990	2.147
Pd@TiO_2:Cr-N	2.863	2.356
O_2-Pd@TiO_2:Cr-N	2.982	2.148

S4: Orbital analysis for the initial stages of O_2 adsorption on pure and co-doped Pd@TiO_2(110)

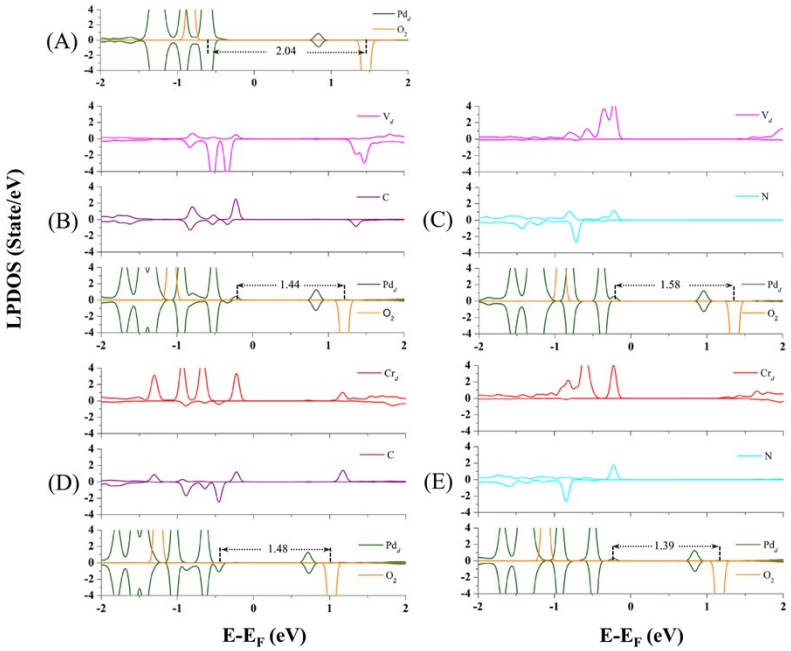

Fig. S3*. (color online): Density of states (DOS) for the initial stages of an O_2 molecule approaching toward (A) Pd@TiO_2(110), and co-doped with (B) V-C, (C) V-N, (D) Cr-C, and (E) Cr-N co-dopant pairs.*

To clearly illustrate the effect of EMSI in improving the chemical activity of the Pd atom via co-doping, we analyze the DOS of the O_2 adsorption on Pd@TiO_2(110) SAC and those co-doped with V-C, V-N, Cr-C, and Cr-N co-dopant pairs when the molecule is far (about 5.0 Å) above the Pd SACs, which can be viewed as the initial stages of the O_2 adsorptions in the present simulations. In general, we can see that the smaller the E_{gap}(HOMO(Pd)-LUMO(O_2)), the larger the E_{ads}(O_2), in close agreement with the well-known *d*-band theory[3, 4]. Note again that, the reduced E_{gap}(HOMO(Pd)-LUMO(O_2)) is originated from an enhanced EMSI through *n-p* co-doping: the stronger the EMSI, the smaller the E_{gap}(HOMO(Pd)-LUMO(O_2)); and consequently the stronger the O_2 activation.

Note that, we have also considered another type of *n*-type co-dopant pair, Cr-S, i.e., one Ti atom is replaced by a Cr atom, and one O is replaced by an S atom. In this situation, we found that Cr-S *n*-type co-doping (see **Fig. S4(A)** for the optimized structure) satisfied with the condition that the HOMO(Pd)-LUMO(O_2) gap is located between the cases of V-N co-doping and Pd@Pristine TiO_2(110). More specifically, in the cases of V-N co-doped and Pd@Pristine-TiO_2(110), the

HOMO(Pd) -LUMO(O_2) gaps are 1.58 and 2.04 eV, respectively, and in the Cr-S co-doped case the HOMO(Pd) -LUMO(O_2) gap is 1.62 eV, as seen from the DOS presented from the **Fig.S4(B)** therein the O_2 is about 5 Å away from the Pd atom. Then, we further examine the O_2 adsorption and CO oxidation on the Cr-S co-doped Pd@TiO_2(110), which is simply denoted as Pd@Cr-S@TiO_2(110). In **Fig. S5**, we present the optimized geometric structure for O_2 adsorption on Cr-S co-doped Pd@TiO_2(110), which is simply denoted as O_2-Pd@Cr-S@TiO_2(110). The calculated adsorption energy of the O_2 molecule ($E_{ads}(O_2)$) on Pd@Cr-S@TiO_2(110) is 0.57 eV, which is well positioned on the linear relationship of the $E_{ads}(O_2)$ as a function of the HOMO(Pd)-LUMO(O_2) gap, as shown in the **Fig. 5** of the main text.

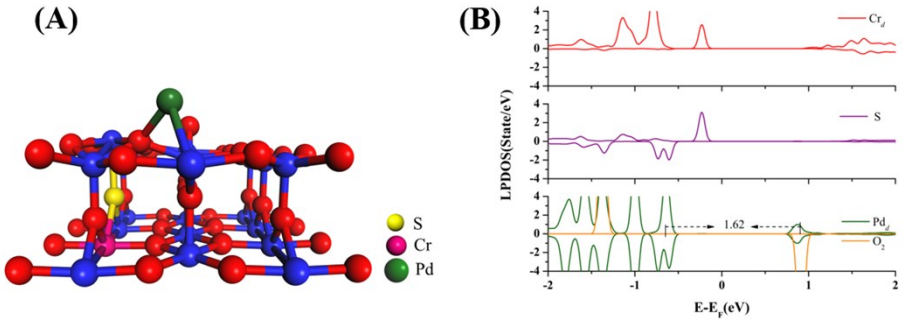

***Fig. S4**: **(A)** Optimized geometric structure of Cr-S co-doped Pd@TiO_2(110),which is simply denoted as Pd@Cr-S@T iO_2(110); **(B)** Local projected density of state (DOS) of the case when an incoming O_2 molecule is about 5 Å high above the deposited Pd atom.*

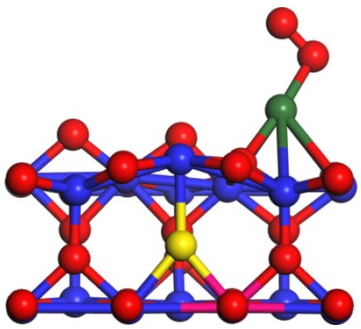

***Fig. S5**: Optimized geometric structure for O_2 adsorption on Cr-S co-doped Pd@TiO_2(110).*

S5: The reason why V-N co-doping slightly departs from the linear trend.

After detailed analysis, we found that (in the **Fig. R3 or Fig. 5**) the reduced reaction barrier for CO oxidation (E_{bar}(CO oxidation)) in V-N co-doping relative to its neighboring cases, such as Cr-C and Cr-S co-doping, can be mainly due to the contrast energy changes upon the local geometric structure relaxations around the Pd single atom during the CO oxidation process.

More specifically, in the following **Fig. S6**, we present the local geometric structures of the initial states (IS) and transition states (TS) of the CO oxidation on Cr-C, V-N, and Cr-S co-doped Pd@TiO_2(110) complexes in the left panels; correspondingly, for both the IS and TS structures, we have also performed static calculations on the energetics of the complexes in which the adsorbed CO and O_2 species are removed, as shown in the right panels. By doing this, we can estimate the geometric effect of the contrast relaxations around the Pd active site on the CO oxidation barriers of the studied systems. One can see that for both the cases of Cr-C and Cr-S co-doping, from the IS to the TS, the energy changes due to the local structural relaxations around the Pd atom are minor, approximately, 0.076 and 0.147 eV; however, for the case of V-N co-doping, the energy change is significant, by about 0.527 eV! Therefore, one can see that it is just such a contrast local geometric relaxation around the Pd single atom during the CO oxidation in the individual case of V-N co-doping as compared to other cases that results in the calculated E_{bar}(CO oxidation) in **Fig. 5** departing from the exactly linear trend.

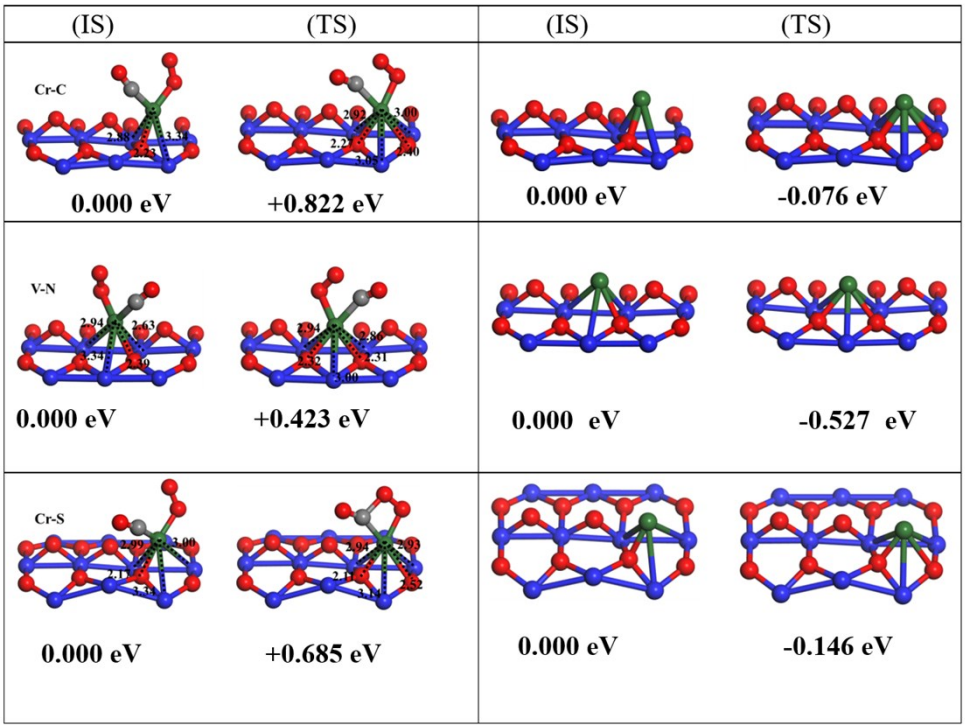

Fig. S6*: Local geometric structures of the initial states (IS) and transition states (TS) for CO oxidation on Cr-C, V-N, and Cr-S co-doped Pd@TiO_2(110) complexes, as shown in the left panels; Correspondingly, in the right panels, for both the IS and TS structures, we have also performed static calculations on the energetics of the complexes in which the adsorbed CO and O_2 species are removed meanwhile kept other atoms possessing the same structures as shown in the left panels.*

1. J. K. Burdett, T. Hughbanks, G. J. Miller, J. W. Richardson and J. V. Smith, *J. Am. Chem.Soc.*, 1987, **109**, 3639-3646.
2. W. Tang, E. Sanville and G. Henkelman, *J. Phys.: Condens. Matter*, 2009, **21**, 084204.
3. B. Hammer, Y. Morikawa and J. K. Norskov, *Phys. Rev. Lett.*, 1996, **76**, 2141-2144.
4. L. P. A. Nilsson, and J. K. Nørskov., *Chemical Bonding at Surfaces and Interfaces*, (Elsevier, Amsterdam, 2008).