

Supporting Information for:

# Monodispersed Pt atoms Anchored on N-doped Graphene as Efficient Catalysts for CO Oxidation: A First-principles Investigation

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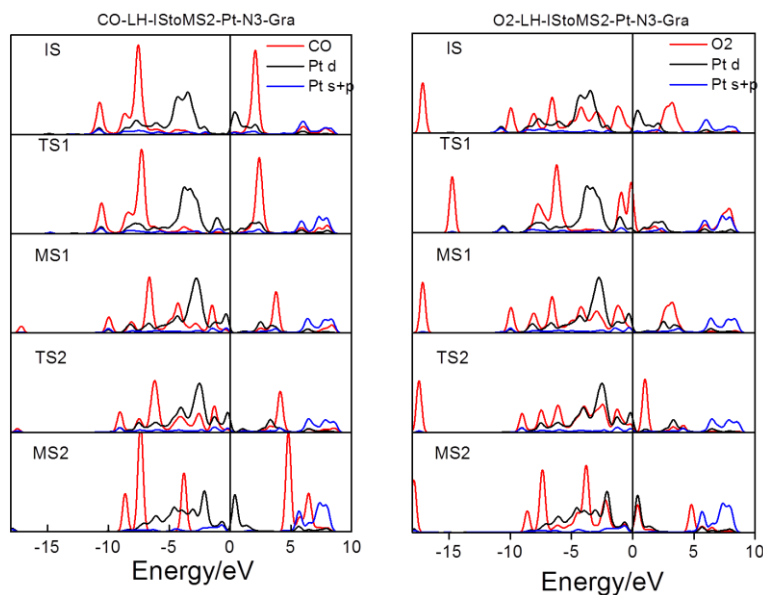


Figure S1. PDOS of CO(left panel),O<sub>2</sub> (right panel) and Pt atom in the LH-IS1, LH-TS1, LH-MS1, LH-TS2 and LH-MS2. The DOS plots were aligned by the calculated Fermi level.

From LH-IS1 to LH-TS1, the DOS peaks of O<sub>2</sub>-1 $\pi$ , O<sub>2</sub>-5 $\sigma$  and O<sub>2</sub>-2 $\pi^*$  states are further downshifted, broadened and overlap with those of CO molecular states, as the result of the evolution of interaction between the coadsorbed molecules. In LH-TS1, as the C-O1 interaction are getting mature, the DOS peaks of O<sub>2</sub> states resonance strongly with those of CO states in the range from -12 eV below E<sub>F</sub> to 2 eV above E<sub>F</sub>. The peak of O<sub>2</sub> state even overlaps with the CO-4 $\sigma$  state, showing that the C-O interaction in CO is significantly weakened and new C-O1 interaction is formed. But these C-O interactions are weak as the resonance between O<sub>2</sub>-2 $\pi^*$  and CO-2 $\pi^*$  of antibonding nature are still strong in the range from -1.5 eV to 1.5 eV. However, the resonance between the CO and O<sub>2</sub> molecular states and Pt-d states of bonding nature is weakened as compared with that in LH-IS1 at about -5 eV, which provides direct evidence for

the interaction between Pt and adsorbed molecules, the instability of LH-TS1 and the tendency for formation of the peroxide-like intermediate (LH-MS1).

Compared with the DOS plot of LH-TS1, the peaks of adsorbates are narrowed in LH-MS1. The DOS peak at -15 eV, originated from the O<sub>2</sub>-4σ state is downshifted and overlaps with the CO states, showing that the C-O1 interaction is further strengthened. The intensity of peaks of O<sub>2</sub> states is enhanced in the range from -10 eV to E<sub>F</sub>, proving that O<sub>2</sub> is activated and C-O1 bonding is stabilized. This is also evidenced by the strong resonance between CO and O<sub>2</sub> states in this energy range. The large broad resonance peak in the range from -7.5 eV to -4.0 eV is split into 2 parts. The part below -5 eV corresponds to the enhanced C-O1 interaction, while the part above -5 eV corresponds to the C-Pt and O<sub>2</sub>-Pt interactions. These occupied states are of bonding nature and contribute to the stability of the peroxide-like intermediate on the embedded Pt atom. The reduced intensity of peaks of partial occupied CO and O<sub>2</sub> antibonding states, which are standing on the E<sub>F</sub> and resonance with the Pt-d states, shows that this peroxide-like intermediate is ready to dissociate by scission of the O1-O2, C-Pt and O-Pt bonds with the involvement of the Pt-d states.

The DOS peaks of the O<sub>2</sub> and CO states standing at the E<sub>F</sub> are split into 2 parts, when the structure evolves from LH-MS1 to LH-TS2. The part that corresponds to the antibonding interaction between C and O1 is shifted upward and hybrids with the Pt-d states, which is a sign of further enhancement of the C-O1 interaction. The part corresponds to the bonding interaction between C-Cu and O1-Pt is downshifted. This synchronizes the formation and desorption of CO<sub>2</sub> over PtN3. During the whole process, the hybridization between the Pt-d states and molecular states of CO and O<sub>2</sub>, proving the significant catalytic role of Pt-d states in coadsorption and subsequent reactions.