Supplementary Information

Density functional study on the CO oxidation reaction mechanism on MnN$_2$-doped graphene

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**Fig. S1** The Fukui function of (a) MnN$_2$C$_2$-hex, (b) MnN$_2$C$_2$-opp and (c) MnN$_2$C$_2$-pen, the isosurface value is 3 e/Å$^3$.

**Table S1** The adsorption energy (eV) of gas on MnN$_2$C$_2$.

|          | MnN$_2$C$_2$-hex | MnN$_2$C$_2$-opp | MnN$_2$C$_2$-pen |
|----------|------------------|------------------|------------------|
| CO$_2$   | −0.292           | −0.270           | −0.260           |
| CO      | −1.448           | −1.318           | −1.424           |
| O$_2$   | −1.778           | −1.975           | −1.655           |
CO + O₂  − 2.490  − 2.283  − 2.327
2CO  − 2.423  − 2.524  − 2.395

Table S2 The energy barriers and reaction energies of CO oxidation along the ER mechanism. ΔE_{bar} represents reaction barrier (eV) and ΔE_{rea} represents reaction energy (eV).

| Model          | Reaction          | ΔE_{bar}(eV) | ΔE_{rea}(eV) |
|---------------|------------------|--------------|--------------|
| MnN₂C₂-hex    | CO₃→O+CO₂       | 0.704        | −0.193       |
|               | O₂+CO→O+CO₂     | 1.101        | −3.620       |
| MnN₂C₂-opp    | CO₃→O+CO₂       | 0.961        | −0.126       |

Fig. S2 Structure of O₂ decomposition reaction on (a) MnN₂C₂-hex and (b) MnN₂C₂-opp. ΔE_{bar} represents reaction barrier (eV) and ΔE_{rea} represents reaction energy (eV).
Fig. S3 Structure of the CO + *O₂ → *CO + *O₂ reaction on (a) MnN₂C₂-hex and (b) MnN₂C₂-pen. ΔE_{bar} represents reaction barrier (eV) and ΔE_{rea} represents reaction energy (eV).
Fig. S4 The second CO is adsorbed on the Mn atom to form structure of two CO co-adsorption on (a) MnN$_2$C$_2$-hex, (b) MnN$_2$C$_2$-opp and (c) MnN$_2$C$_2$-pen. ΔE$_{\text{bar}}$ represents reaction barrier (eV) and ΔE$_{\text{rea}}$ represents reaction energy (eV).
Fig. S5 Structure of the oxidation of CO on MnN$_2$C$_2$-pen along the LH and TER mechanisms.

Fig. S6 Structure of the oxidation of CO on MnN$_2$C$_2$-hex along the LH and TER mechanisms.
Fig. S7 Molecular dynamics trajectory of intermediate product OCOO spontaneously decomposes into O and CO₂ on MnN₂C₂-hex at 350 K with snapshots of intermediates at different times.