Supporting Information for

"Metal single-atom coordinated graphitic carbon nitride as an efficient catalysts for CO Oxidation"

Shiyan Wang[a], Jiaqi Li[b], Qiang Li*[,a], Xiaowan Bai[a] and Jinlan Wang*[,a]

[a]School of Physics, Southeast University, Nanjing 211189, China.

[b]College of Chemistry and Chemical Engineering, Hunan University, Changsha, Hunan 410082, China

*E-mail: qiang.li@seu.edu.cn; jlwang@seu.edu.cn

Computational details

The binding energy of Co atom on g-C_3N_4 are calculated by means of the following equations

$$E_b = E_{M/sub} - E_{sub} - (E_{M(bulk)}/n)$$

where the $E_{M/sub}$ and E_{sub} are the energies of Co/g-C_3N_4 and g-C_3N_4, respectively. The $E_{M(bulk)}$ is the energy of Co bulk and n is the number of Co atoms in its bulk.

The adsorption energies (E_{ads}) of the adsorbate (O_2, CO, etc.) are calculated by means of the following equations

$$E_{ads} = E_{slab} + E_{adsorbate} - E_{adsorbate/slab}$$

where E_{slab}, $E_{adsorbate}$ and $E_{adsorbate/slab}$ represent the total energies of the clean slab, the isolated adsorbed atom/molecule and the slab after adsorption, respectively. With this definition, a positive value of E_b or E_{ads} indicates that the adsorption is exothermic. The activation energy barriers for CO oxidation were calculated according to the following formula

$$E_{act} = E_{TS} - E_{IS}$$

where E_{TS} and E_{IS} are energies of the transition state and initial state, respectively.

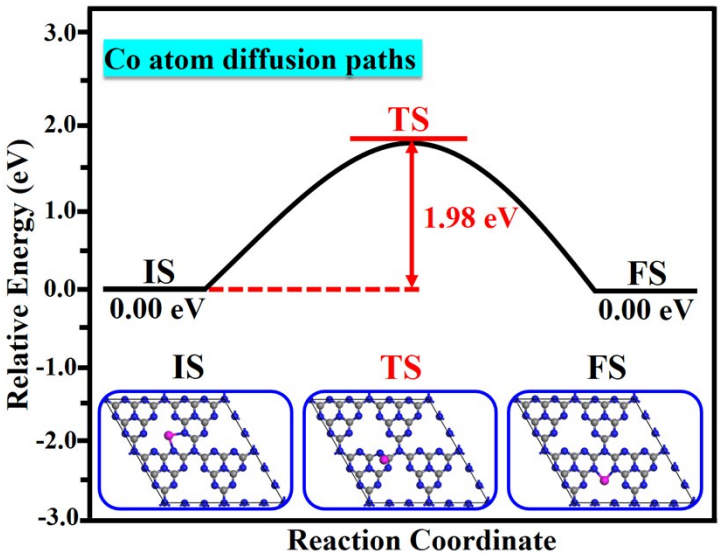

Fig. S1 The most probable diffusion path of Co atom on g-C_3N_4. The most stable adsorption site as the initial states (IS) and the adjacent of the most stable adsorption site as the final states (FS).

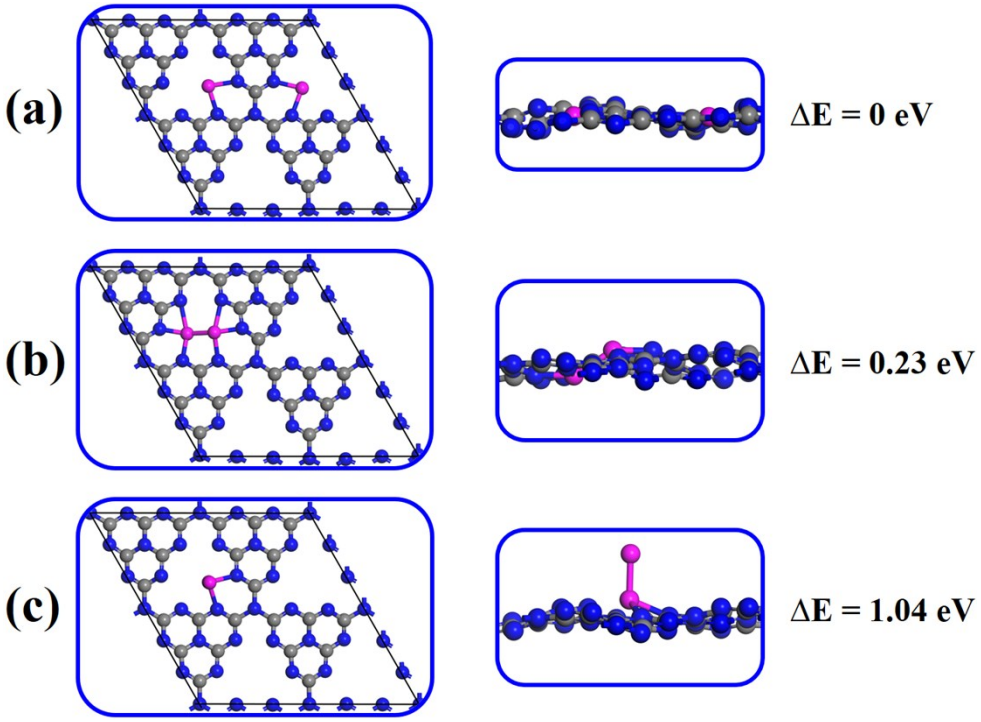

Fig. S2 (a) Two cobalt atoms are scattered at two sites, **(b)** Co dimer adsorbed at single hole and parallel to the plane and **(c)** Cobalt dimers adsorbed at the one site and vertical to the plane of the g-C_3N_4, insert are top and side views of the snapshot of atomic configuration. The relative energy (ΔE) is calculated with respect to **Fig. S2a**.

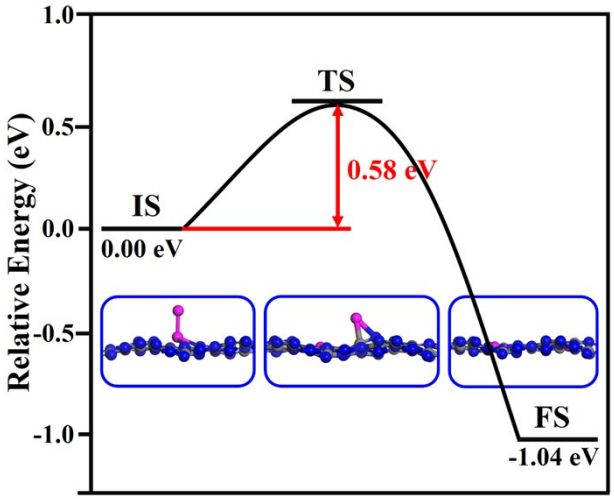

Fig S3. Atomic configurations for the dissociation of the Co dimer of the Co_2/g-C_3N_4 catalyst to form two separated Co monomers at two sites, including IS, TS, and FS.

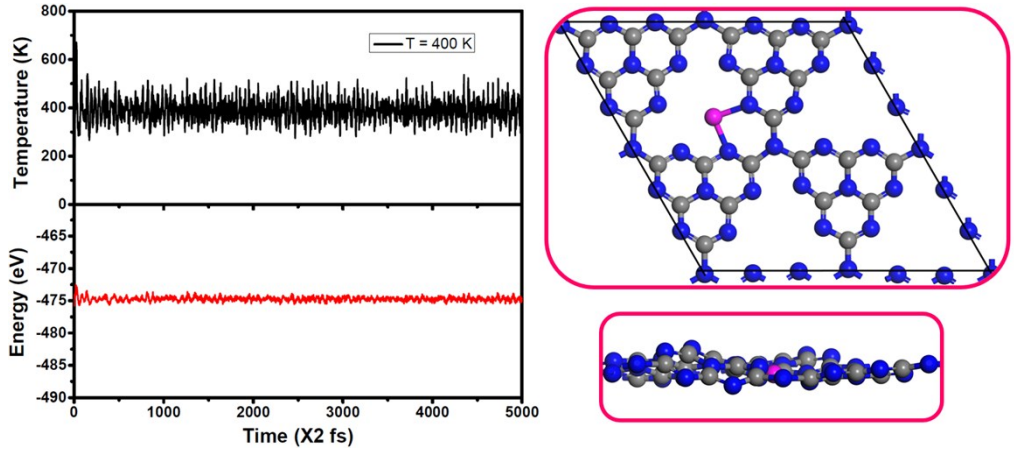

Fig. S4 Variations of temperature and energy of against the time for the AIMD simulations of Co/g-C_3N_4, insert are top and side views of the snapshot of atomic configuration. The simulation is run under 400 K for 10 ps with a time step of 2 fs.

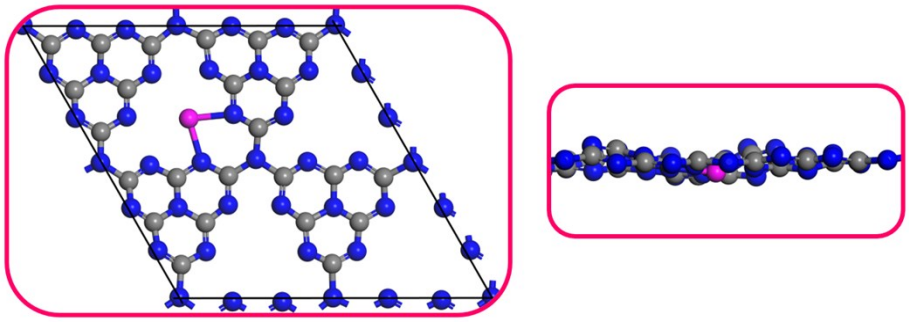

Fig. S5 The AIMD simulations of Co/g-C_3N_4, insert are top and side views of the snapshot of atomic configuration. The simulation is run under 600 K for 10 ps with a time step of 2 fs.

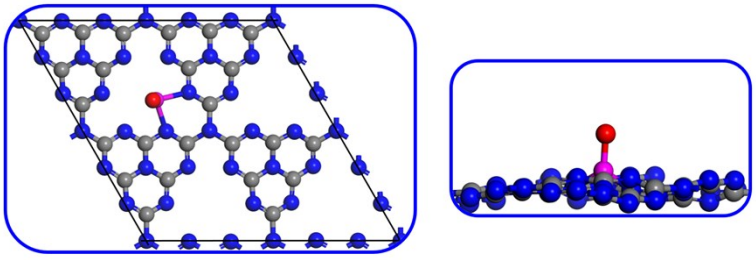

Fig. S6 The adsorption of O on Co/g-C_3N_4, including the top and side views of atomic configuration.

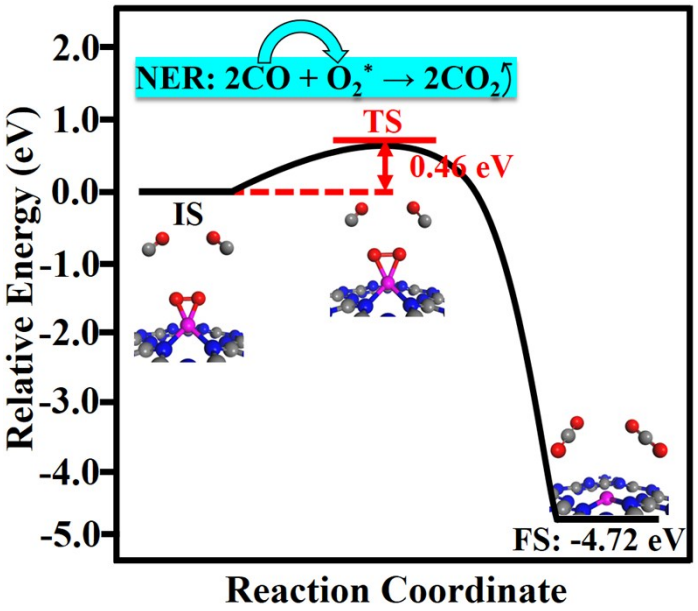

Fig. S7 Minimum energy profiles and the configuration of different states including the IS, TS and FS for CO oxidation on Co/g-C_3N_4. NER mechanism: $2CO + O_2^* \rightarrow 2CO_2$.

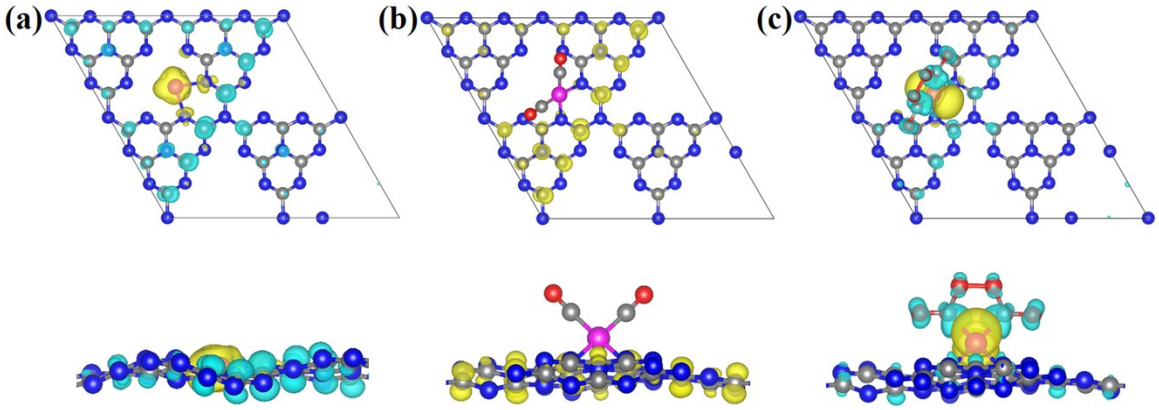

Fig. S8 Top view and side view of spin density of the Co single atom during the CO oxidation process *via* TER mechanism. **(a)** Co/g-C_3N_4, **(b)** 2CO and **(c)** OCOOCO* intermediate adsorbed on Co/g-C_3N_4. The isosurface value is set to 1×10^{-3} eÅ^{-3}.

Table S1. The energy of different states including the IS, TS and FS for CO oxidation on Co/g-C_3N_4 *via* corresponding mechanisms. The energy of the IS corresponding to the adsorption energy.

ER	**(a)** $CO + O_2^* \rightarrow O^* + CO_2$	E_{IS}		E_{TS}		E_{FS}		E_{act1}
		-2.15		-1.90		-4.68		0.25
	(b) $CO + O^* \rightarrow CO_2$	E_{IS1}		E_{TS1}		E_{FS1}		E_{act2}
		-1.39		-0.99		-3.33		0.40
LH	**(a)** $O_2^* + CO^* \rightarrow O^* + CO_2$	E_{IS}		E_{TS}		E_{FS}		E_{act1}
		-3.26		-3.16		-4.91		0.10
	(b) $O^* + CO^* \rightarrow OCO^* \rightarrow CO_2$	E_{IS1}	E_{TS1}	E_{MS}	E_{TS2}	E_{FS1}	E_{act2}	E_{act3}
		-2.71	-2.63	-3.76	-3.17	-3.99	0.08	0.59
NER	**I.** $2CO + O_2^* \rightarrow 2CO_2$	E_{IS}		E_{TS}		E_{FS}		E_{act1}
		-2.14		-1.68		-6.86		0.46
	II. $2CO + O_2^* \rightarrow OOCCOO^* \rightarrow 2CO_2$	E_{IS}	E_{TS1}	E_{MS}	E_{TS2}	E_{FS}	E_{act2}	E_{act3}
		-2.14	-1.91	-6.43	-6.08	-6.86	0.23	0.35
TER	$O_2 + 2CO^* \rightarrow OCOOCO^* \rightarrow 2CO_2$	E_{IS}	E_{TS}	E_{MS}	E_{TS1}	E_{FS}	E_{act1}	E_{act2}
		-3.24	-3.07	-3.61	-3.40	-6.85	0.17	0.21