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# Multiscale porous single-atom Co catalysts for epoxidation by $O_2$

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**Theoretical method**

The DFT calculations were performed with Quantum Espresso (QE) software[1] which uses a plane wave basis set. The electron exchange-correlation was processed with the framework of generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof (PBE) parametrization.[2] The electron-ion interaction was described using the projected augmented wave (PAW) method.[3] The spin is unristricted. The kinetic energy cutoffs of the plane wave and electron density were 80 and 500 Ry, respectively. For the calculation of bulk CoO, an 8 x 8 x 8 k-grid was used for the sampling in the Brillouin zone. Then, a (2 x 2) 5 layers CoO (001) slab model was build. For the calculation of CoO (001) slab model, a 3 x 3 x 1 k-grid was used. The Co embedded nitrogen-doped graphene model were modeled based on a 6 x 6 x 1 hexagonal suercell of graphene. Co atom was coordianted with three N atoms and one C atom (Co-$N_3$). For the calculation of Co-$N_3$, a 1 x 1 x 1 gamma k-point was used. Energy convergence of $10^{-7}$ eV/atom was ensured during the self-consistent field calculations. And the convergence criteria for the atomic forces was 0.05 eV/Å. The adsorption energy of O was calculated according to the following equation,

$E_{ad}=E_{slab-O} -E_{slab} -1/2\ E_{O2}$

Where $E_{slab-O}$ is the energy of slab model with a O atom adsorbed on it; $E_{slab}$ is the energy of slab model and $E_{O2}$ is the energy of $O_2$ molecule.

**References:**


1. Giannozzi, P.; Baroni, S.; Bonini, N.; Calandra, M.; Car, R.; Cavazzoni, C.; Ceresoli, D.; Chiarotti, G. L.; Cococcioni, M.; Dabo, I.; Dal Corso, A.; de Gironcoli, S.; Fabris, S.; Fratesi, G.; Gebauer, R.; Gerstmann, U.; Gougoussis, C.; Kokalj, A.; Lazzeri, M.; Martin-Samos, L.; Marzari, N.; Mauri, F.; Mazzarello, R.; Paolini, S.; Pasquarello, A.; Paulatto, L.; Sbraccia, C.; Scandolo, S.; Sclauzero, G.; Seitsonen, A. P.; Smogunov, A.; Umari, P.; Wentzcovitch, R. M., *J Phys Condens Matter* **2009,** 21 (39), 395502.
2. Perdew, J. P.; Burke, K.; Ernzerhof, M., *Phys. Rev. Lett.* **1996,** 77 (18), 3865.
3. Dal Corso, A., *Comp. Mater. Sci.* **2014,** 95, 337-350.

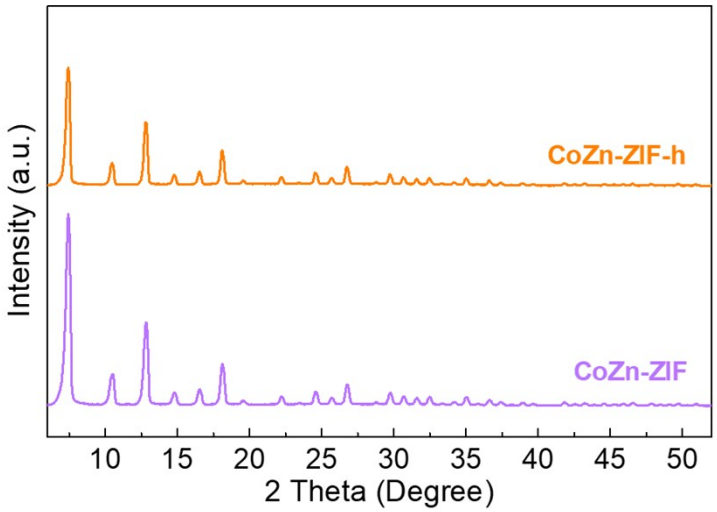


**Figure S1.** XRD patterns of CoZn-ZIF and CoZn-ZIF-h precursors.

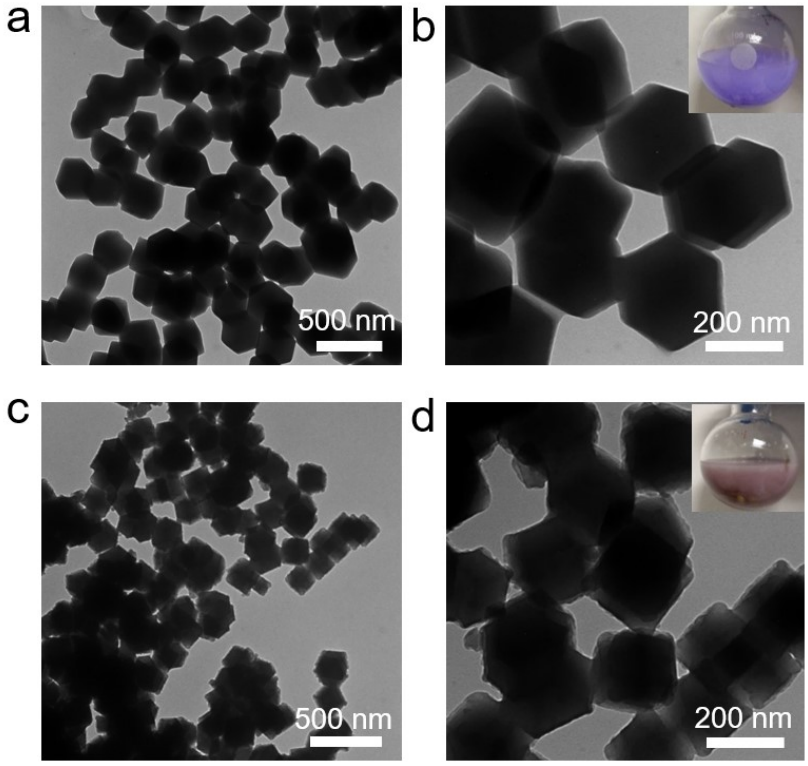


**Figure S2.** (a) Low-magnification and (b) high-magnification TEM images of the CoZn-ZIF precursors. (c) Low-magnification and (d) high-magnification TEM images of the CoZn-ZIF-h precursors.

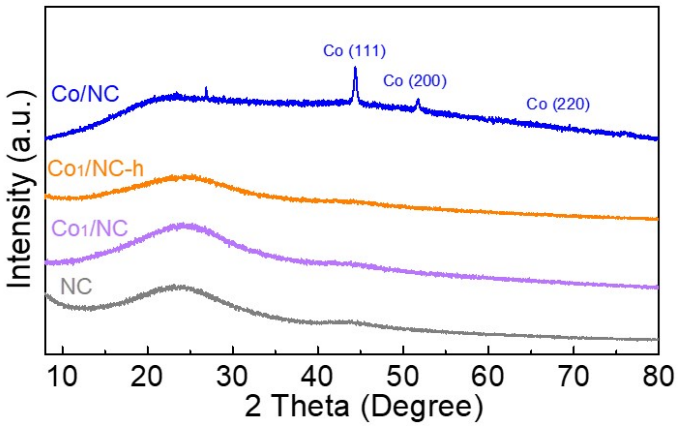


**Figure S3.** XRD patterns of the Co/NC, $Co_1$/NC-h, $Co_1$/NC and NC catalysts. Note: Reflection peaks of Co/NC was well consistent with the standard metallic Co (PDF # 15-0806)). Meanwhile, the peak at around 27° for Co/NC catalyst might be assigned to the phase of $Co_2O_3$ (PDF # 02-0770), due to the uncoated metallic Co being easily oxidized by air.

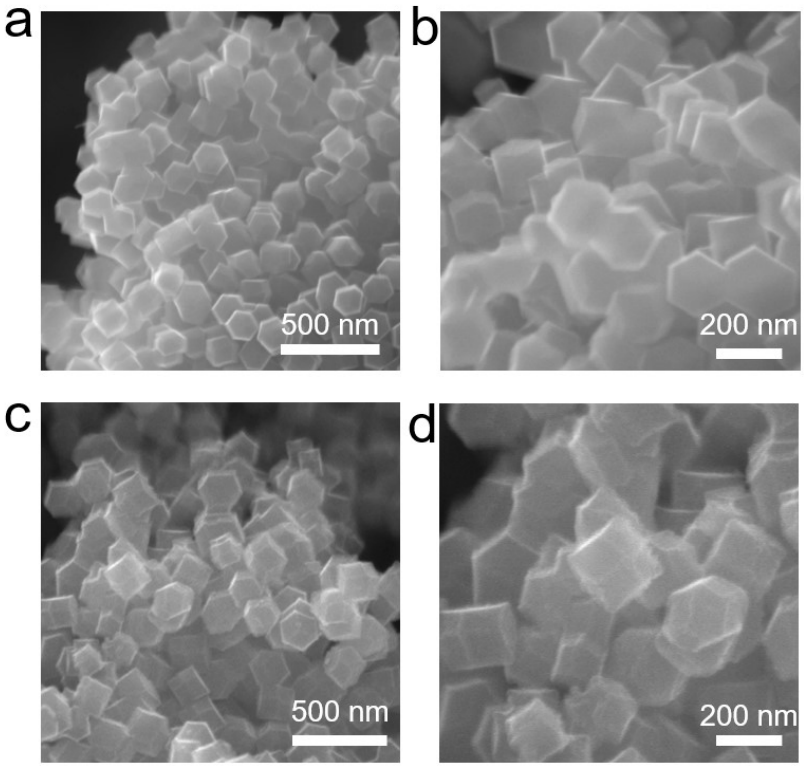


**Figure S4.** (a) Low-magnification and (b) high-magnification SEM images of the $Co_1$/NC catalysts. (c) Low-magnification and (d) high-magnification TEM images of the $Co_1$/NC-h catalysts.

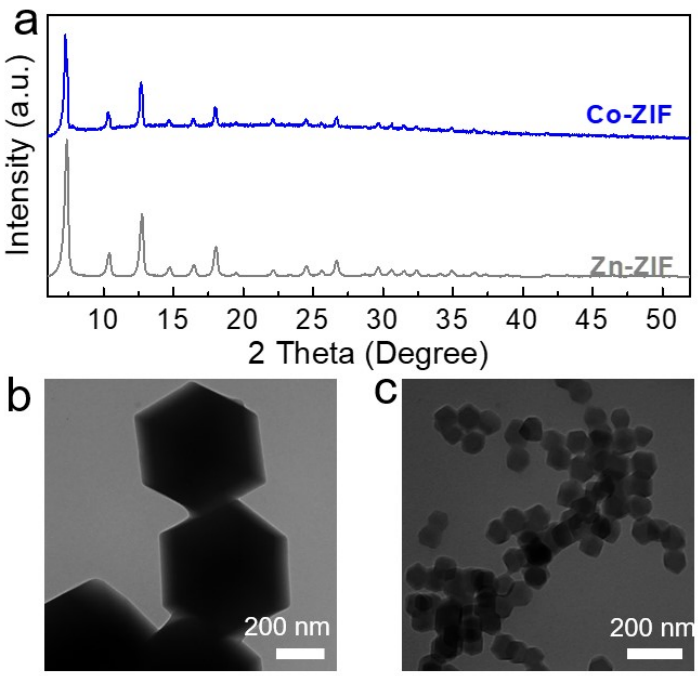


**Figure S5.** (a) XRD patterns of Co-ZIF and Zn-ZIF precursors. TEM images of (b) Co-ZIF and (c) Zn-ZIF precursors.

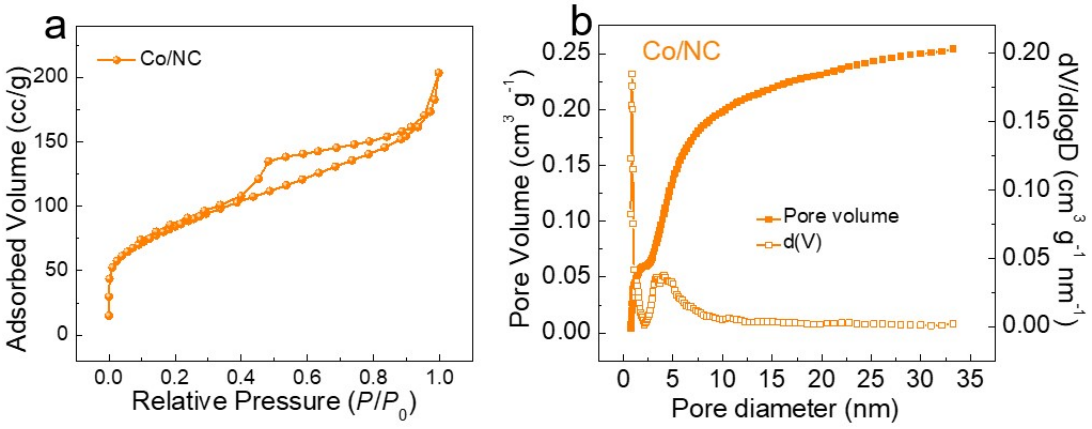


**Figure S6.** (a) $N_2$ adsorption-desorption isotherms curve and (b) pore volume and pore size distribution of Co/NC catalysts.

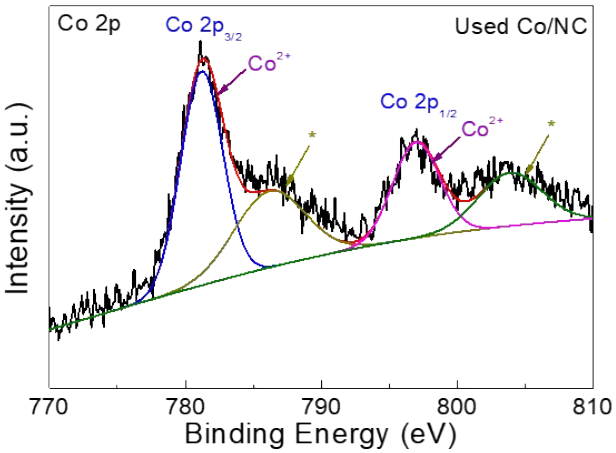


**Figure S7.** XPS analysis of Co 2p peaks of used Co/NC catalysts.

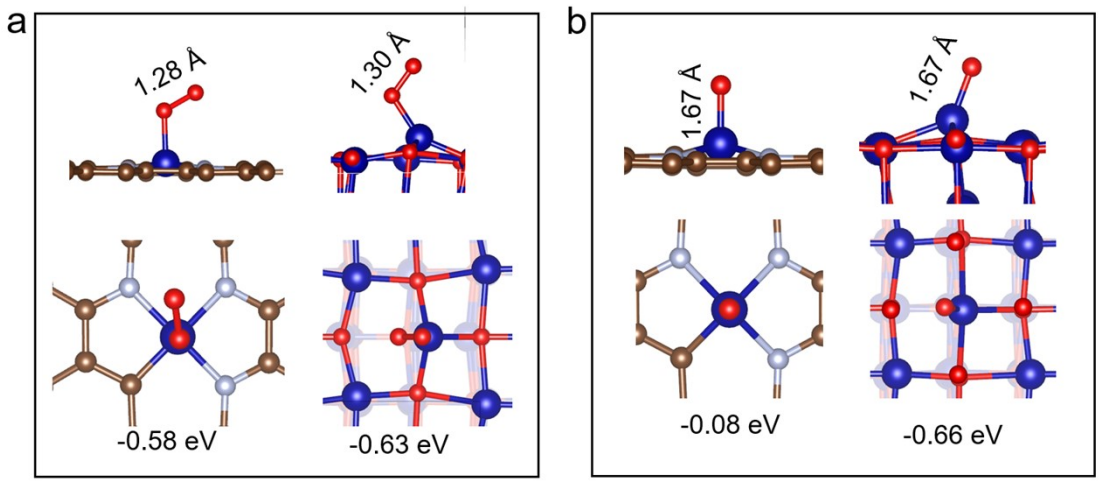


**Figure S8.** Adsorption behaviour of (a) $O_2$ molecule and (b) O atom on the Co-$N_3$ and CoO surface. Red: O atom, dark blue: Co atom, and dark brown: C atom.

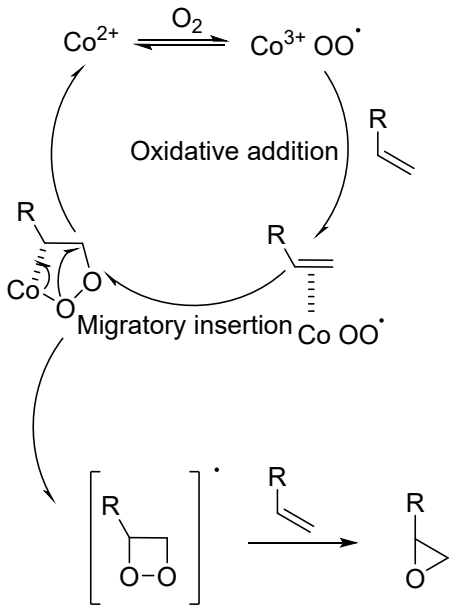


**Figure S9**. The possible reaction process of single-atom Co for the alkene epoxidation.

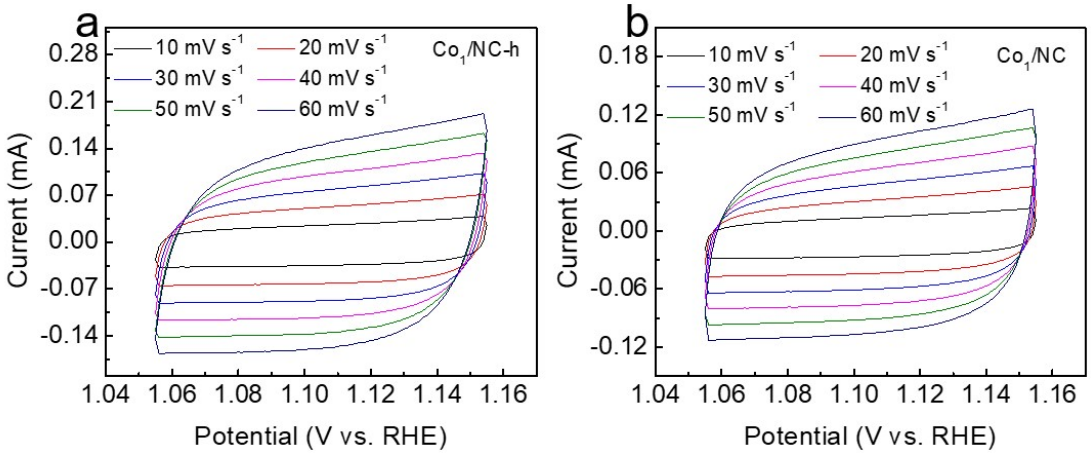


**Figure S10**. CV curves measured from 10 to 60 mV/s for the (a) $Co_1$/NC-h and (b) $Co_1$/NC catalysts.

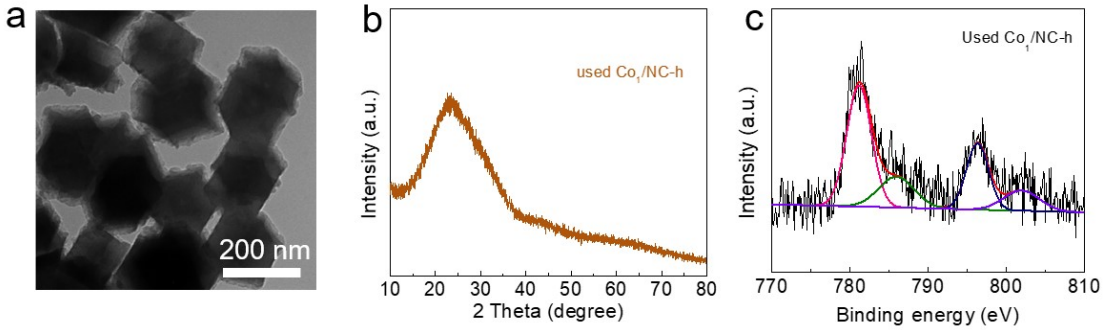


**Figure S11.** (a) TEM image, (b) XRD pattern and (c) XPS analysis for Co 2p peak of used $Co_1$/NC-h catalysts.

**Table S1.** Summary of the epoxidation performances by various catalysts.

| Catalysts | Substrate | Temp. | $O_2$ (bar) | Time (h) | Conv. | Sel. | Ref. |
|---|---|---|---|---|---|---|---|
| $Fe_2$/mpg-$C_3N_4$ | *trans*-stilbene | 90 | 1 atm $O_2$ | 24 h | 91 | 93 | *Nat. Commun*., **2018**, 9(1), 1-7. |
| $Fe_1$/mpg-$C_3N_4$ | *trans*-stilbene | 90 | 1 atm $O_2$ | 24 h | trace | | *Nat. Commun*., **2018**, 9(1), 1-7. |
| $Pt_2$/mpg-$C_3N_4$ | Styrene | 100 | 1 atm $O_2$ | 12 h | 93 | 78 | *Nat. Commun*., **2021**, 12(1): 1-9. |
| $Ag_1$-$C_2N_1$ | Styrene | 100 | 1 atm $O_2$ | 12 h | 96 | 81 | *ACS Catal*. **2021**, 11, 4946−4954. |
| SAS-Fe | Styrene | 140 | 1 atm $O_2$ | 3 h | 64 | 89 | *Adv. Mater*. **2020**, 32, 2000896 |
| Co-N-C/$SiO_2$ | Methyl oleate | 35 | 1 atm $O_2$ | 5 h | 99 | 99 | *J. Chem. Phys*., **2021**,154(13):131103. |
| DUT-5-BPyDC(10)-Co | *trans*-stilbene | 150 | Air(200ml/min), | 24 h | 95 | 70 | *ChemCatChem*. **2020**, 12, 1134–1142 |
| Pd/γ-AlOOH | *trans*-stilbene | 120 | 1 atm $O_2$ | 4 h | 84 | 99 | *Chem. Eng. J*., **2022**, 429: 132149. |
| Mn-2@POP-20 | Chalcone | r.t. | $H_2O_2$/acid DMBA | 2 h | 93 | 96 | *ACS Catal*., **2021**, 11, 10964−10973. |