# Supporting information

Fangying Zhang,[a+] Wangwang Fang,[c+] Fanyong Yan,[b] Bowei Wang,[*adef] Dan Zhang,[a] Tao Wang,[a] Guoyi Bai,[g] Ligong Chen,[adef] Yang Li [adef] and Xilong Yan[*adef]

[a]. *School of Chemical Engineering and Technology, Tianjin University, Tianjin 300350, P. R. China.*

[b]. *Tianjin Key Laboratory of Green Chemical Engineering Process Engineering， Tiangong University, Tianjin 300387, P. R. China.*

[c]. *Shaoxing Xingxin New Material Co., Ltd., Shaoxing 312369, P. R. China*

[d]. *Institute of Shaoxing, Tianjin University, Zhejiang 312300, P. R. China..*

[e]. *Tianjin Engineering Research Center of Functional Fine Chemicals, Tianjin, P. R. China.*

[f]. *Guangdong Laboratory of Chemistry and Fine Chemical Industry Jieyang Center, Guangdong Province 522000, P. R. China*

[g]. *Key Laboratory of Chemical Biology of Hebei Province, College of Chemistry and Environmental Science, Hebei University, Baoding 071002, P. R. China*

*+ These authors contributed equally to this work.*

**Corresponding authors. E-mail: bwwang@tju.edu.cn (Bowei Wang); yan@tju.edu.cn (Xilong Yan)*

**Materials**

Except as otherwise noted, all chemicals and reagents were of analytical grade and used without further purification. Cerium nitrate hexahydrate was supplied by Meryer Chemical Technology Co., Ltd. Chitosan was supplied by Sun Chemical Technology Co., Ltd. Methyl phenyl sulfide was purchased from Ailan (Shanghai) Chemical Technology Co., Ltd. Methyl phenyl sulfoxide was purchased from Jiuding Chemical (Shanghai) Technology Co., Ltd. Cobalt oxalate was purchased from Tianjin Kermel Chemical Technology Co., Ltd.

**Characterization**

Scanning electron microscopy (SEM) was recorded by performed on a Hitachi S-4800 microscopy. Elemental analysis (EA) results were provided from avario MICRO cube element analyzer (Elementar, Germany). Elemental analysis was measured by inductar EL cube elemental analyzer and Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) was determined by Vista-MPX spectrometer. The specific surface area was carried out using the Brunauer-Emmer-Teller (BET) method with nitrogen physisorption at a liquid nitrogen temperature on NOVA 2000e analyzer (Quantachrome, U.S.A.). Transmission electron microscope (TEM) images were performed on a JEOL JEM-2100F microscope. Scanning transmission electron microscopy (STEM) images were recorded by energy dispersive spectrometer (EDS; EDAX PV6761/55). The results of X-ray diffraction (XRD) patterns were obtained by a Rigaku SmartLab X-Ray Diffraction 9 kW with a Cu-Kα X-ray source in the range of 5-80°. The X-ray photoelectron

spectroscopy (XPS) measurements were detected by EscaLab Xi+ spectrometer. Raman spectra were collected by DXR Microscope (Thermo Scientific, U.S.A.).

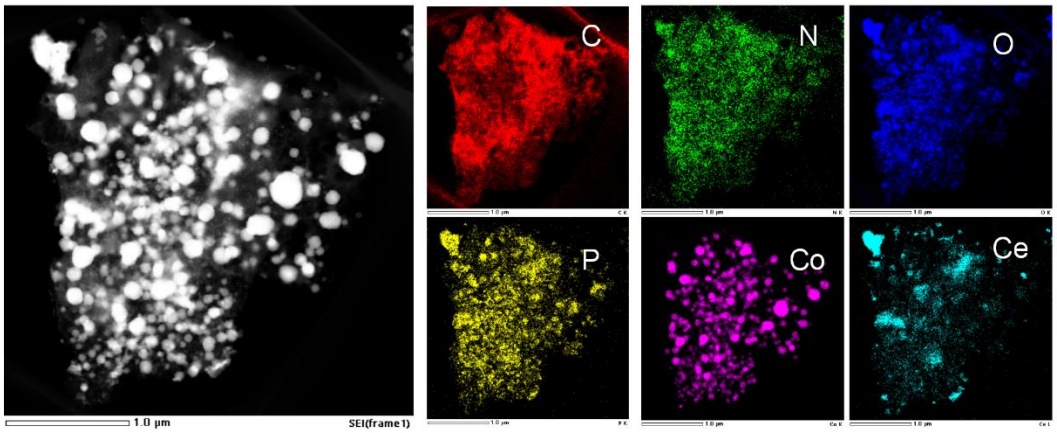


**Figure S1**. STEM images of $CoCe_2$/N-C.

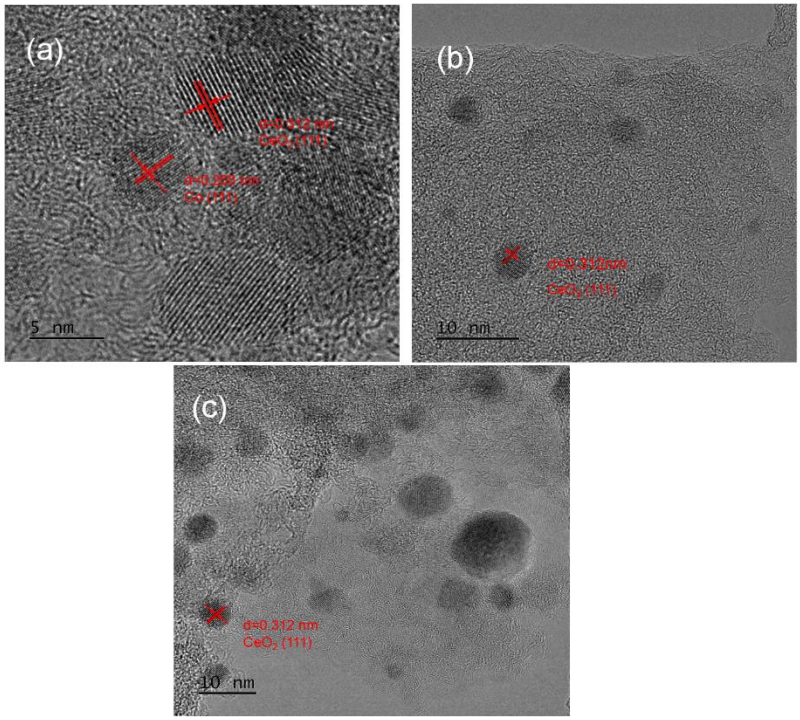


**Figure S2**. HRTEM images of $CoCe_2$/N-C, $CoCe_3$/N-C, $CoCe_5$/N-C.

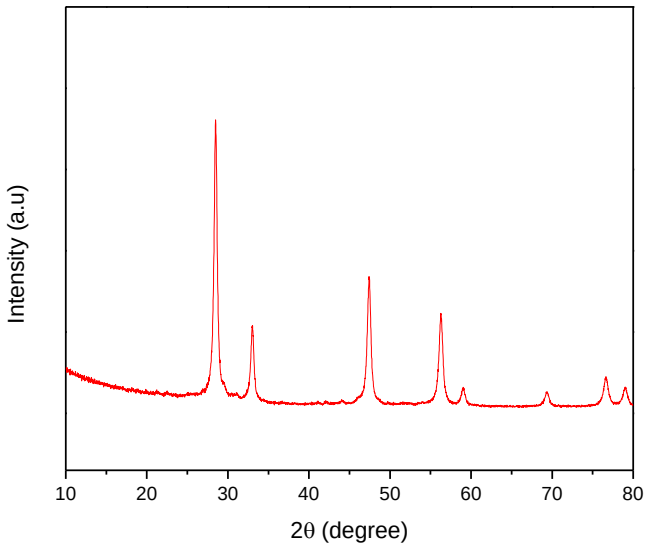


**Fig. S3**. XRD patterns of $CeO_2$

**Table S1**. The relative cotent of N species of $CoCe_x$/N-C.

| Catalyst | N species relative cotent | | | |
|---|---|---|---|---|
| | Pyridinic-N(%) | $CoN_x$(%) | Pyrrolic-N(%) | Graphite-N(%) |
| $CoCe_2$/N-C | 21.20 | 17.11 | 24.94 | 36.75 |
| $CoCe_3$/N-C | 36.99 | 20.67 | 26.06 | 16.28 |
| $CoCe_4$/N-C | 36.19 | 22.08 | 23.97 | 17.76 |
| $CoCe_5$/N-C | 34.23 | 16.92 | 23.14 | 25.70 |
| $CoCe_6$/N-C | 24.74 | 17.07 | 22.17 | 36.02 |

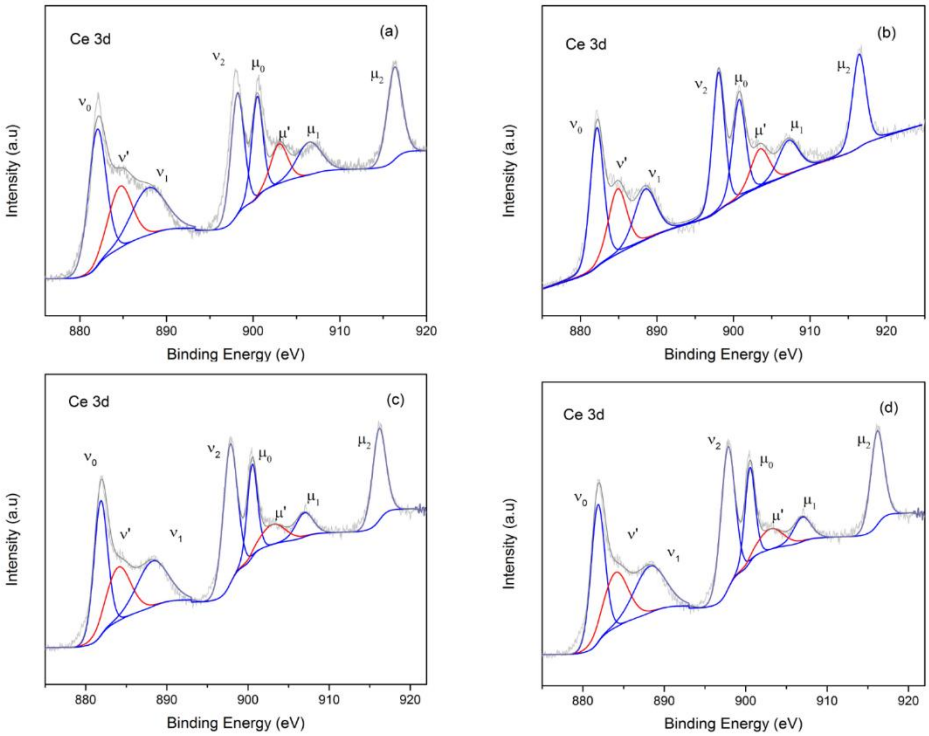


**Fig S4**. Ce 3d spectra of $CoCe_2$/N-C (a), $CoCe_4$/N-C (b), $CoCe_5$/N-C (c), $CoCe_6$/N-C (d)

**Table S2**. The content ratios of $Ce^{3+}$ and $Ce^{4+}$ ($Ce^{3+}/Ce^{4+}$) in $CoCe_x$/N-C catalyst

| catalyst | $CoCe_2$/N-C | $CoCe_3$/N-C | $CoCe_4$/N-C | $CoCe_5$/N-C | $CoCe_6$/N-C |
|---|---|---|---|---|---|
| $Ce^{3+}/Ce^{4+}$ | 0.23 | 0.26 | 0.24 | 0.23 | 0.23 |

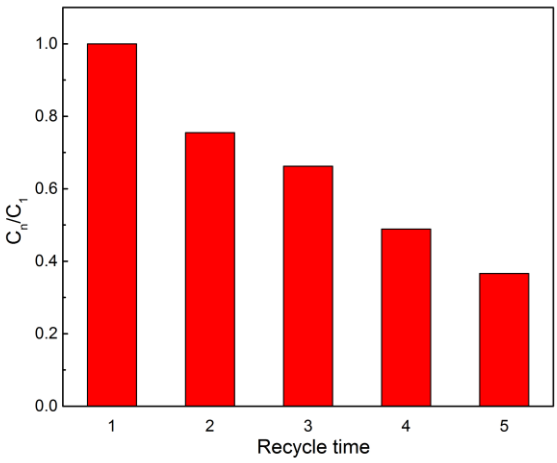


**Figure S5**. Stability test of Pd/C for hydrogenation of methyl phenyl sulfoxide.

Reaction conditions: 0.125 mmol methyl phenyl sulfoxide, 4.5 mol% catalyst, 2 mL ethanol, 80 ℃, 1 MPa $H_2$, 2 h.

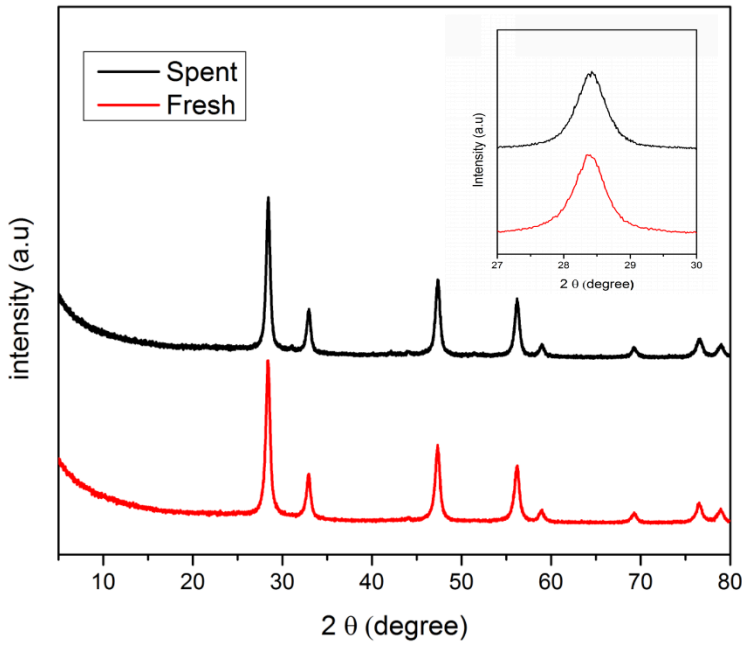


**Figure S6**. XRD patterns of fresh and used $CoCe_3$/N-C.

**Table S3.** Metal content of fresh and used $CoCe_3$/N-C

| Catalyst | Co content (wt%) | Ce content (wt%) |
|---|---|---|
| $CoCe_3$/N-C | 0.82 | 19.98 |
| $CoCe_3$/N-C (used) | 0.80 | 19.79 |