Dual-active sites of Co and oxygen vacancy in Co-doped CeO$_2$ catalyzed toluene oxidation for consequent Knoevenagel condensation

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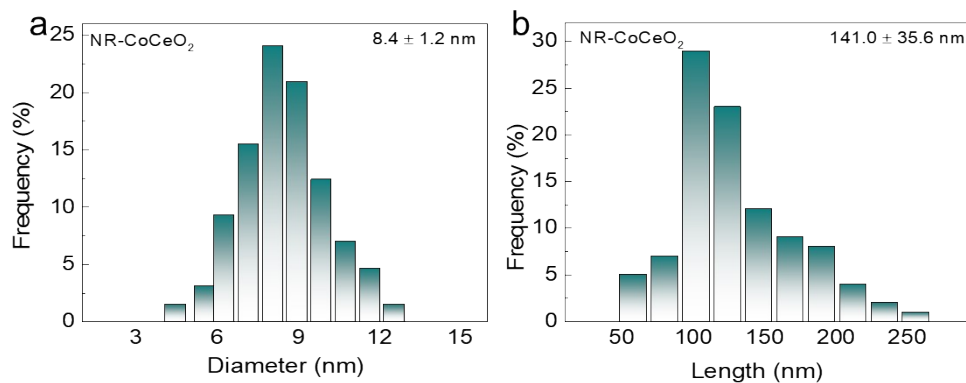**E-mail:** zhangsai1112@nwpu.edu.cn and yongquan@nwpu.edu.cn

Figure S1. The (a) diameter and (b) length of the NR-CoCeO₂ catalysts.
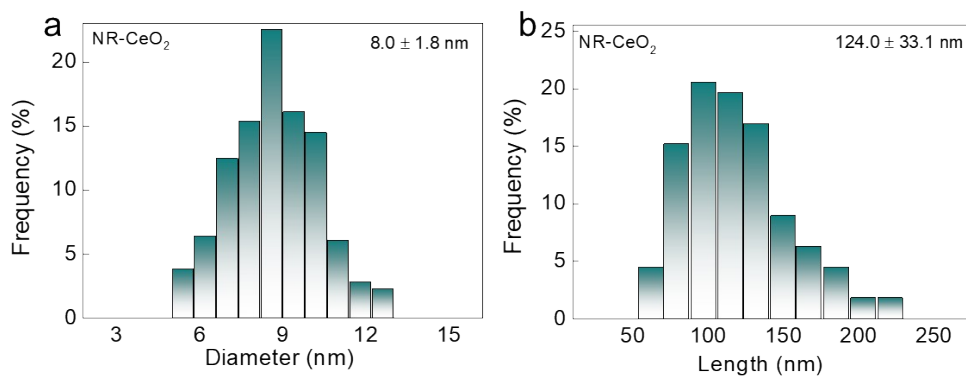

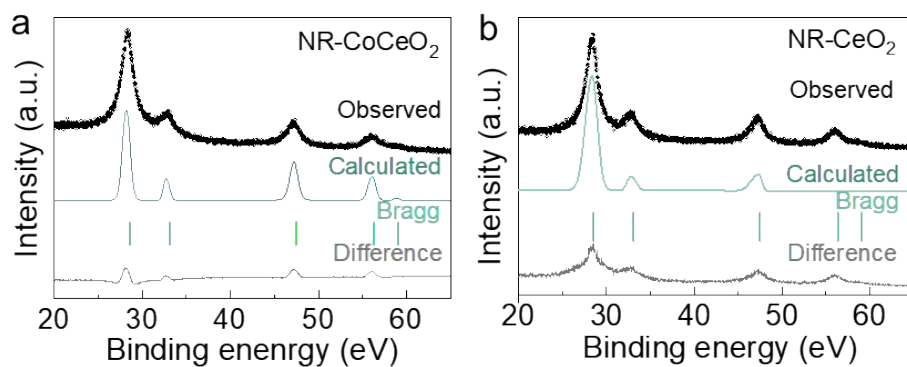**Figure S2.** The (a) diameter and (b) length of the NR-CeO₂ catalysts.

Figure S3. Rietveld refinement XRD analysis of (a) NR-CoCeO₂ and (b) NR-CeO₂.
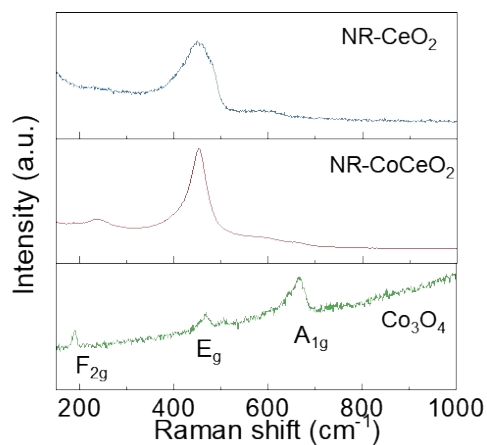
Figure S4. Raman profiles of NR-CoCeO$_2$, NR-CeO$_2$ and Co$_3$O$_4$ catalysts.
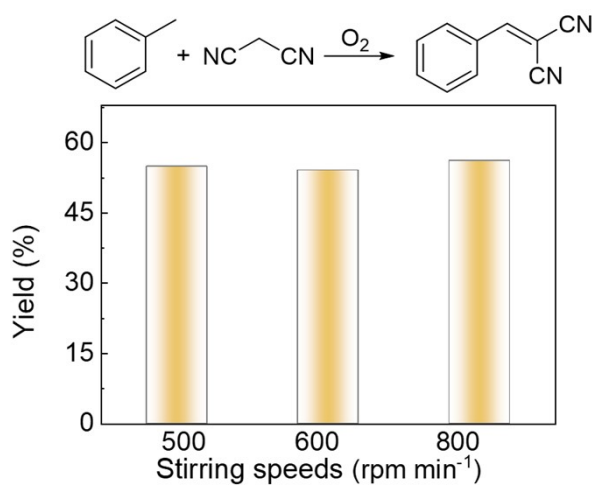

Figure S5. The influence of stirring speeds on catalytic preformation of the tandem transformation of toluene and malononitrile into benzylidenemalononitrile. **Reaction conditions:** toluene (2.0 mL), malononitrile (0.5 mmol), catalysts (5.0 mg), 140 °C and 0.5 MPa O$_2$.
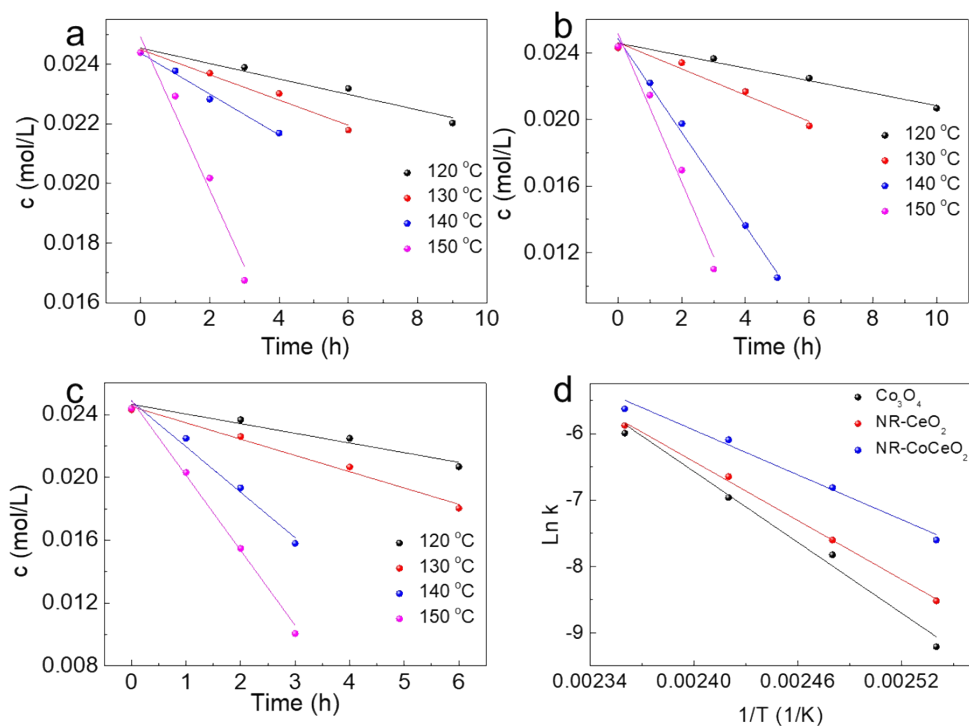
Figure S6. Catalytic behavior of (a) Co_3O_4, (b) NR-CeO$_2$ and (c) NR-CoCeO$_2$ for the tandem transformation of toluene and malononitrile into benzylidenemalononitrile at various reaction temperatures. (d) And the plot of ln$k$ as function of ($1/T$) for Co_3O_4, NR-CeO$_2$ and NR-CoCeO$_2$ catalyzed transfer of toluene and malononitrile into benzylidenemalononitrile. **Reaction conditions**: toluene (2 mL), malononitrile (0.5 mmol), catalysts (5 mg) and 0.5 MPa O_2.
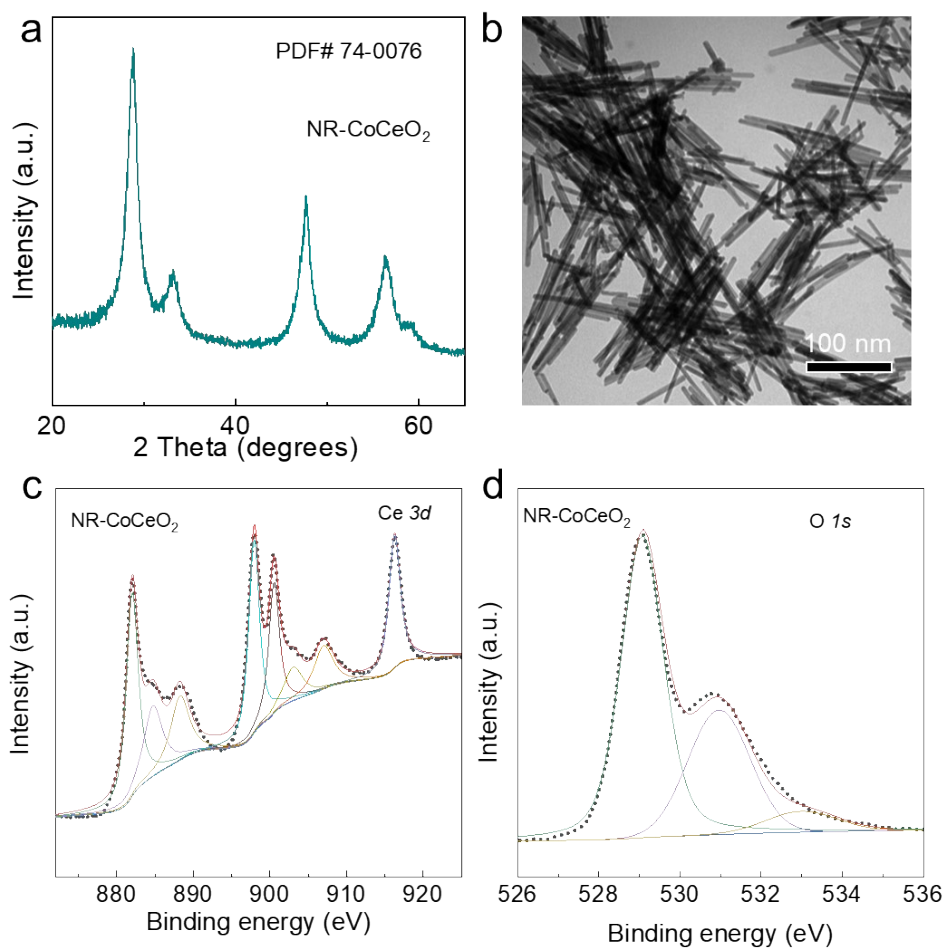
Figure S7. (a) XRD pattern, (b) TEM image, and XPS analysis of (c) Ce *3d* and (d) O *1s* for the used NR-CoCeO₂ catalysts.
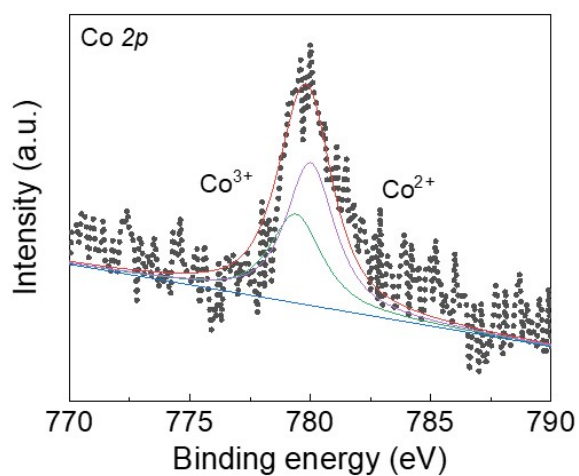

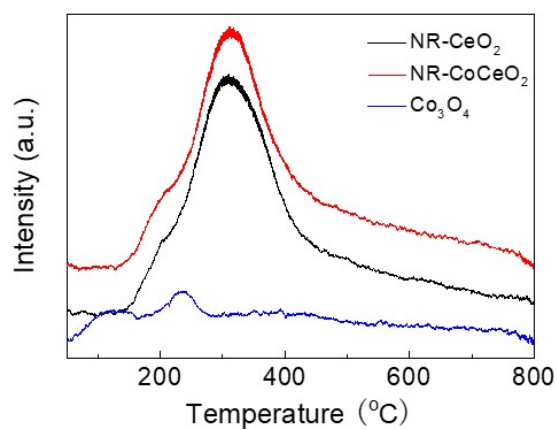**Figure S8.** XPS analysis of Co *2p* for the NR-CoCeO₂ catalysts.

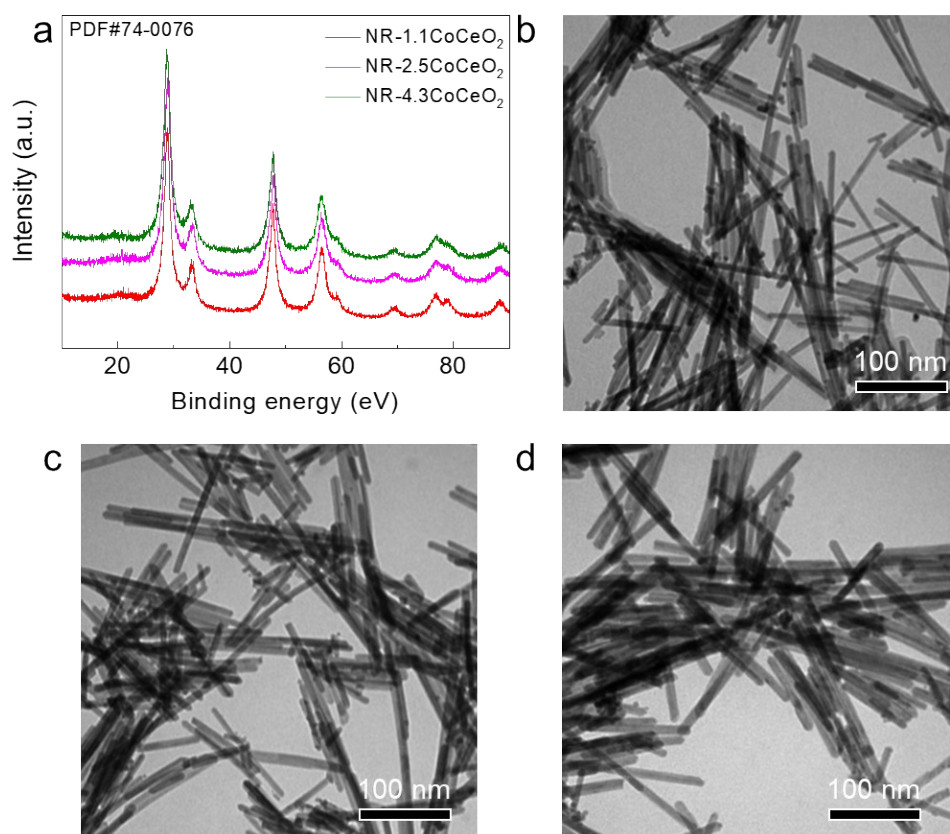**Figure S9**. The capability to activate O_2 of NR-CeO$_2$, NR-CoCeO$_2$ and Co$_3$O$_4$ catalysts.

Figure S10. (a) XRD pattern and TEM images for the NR-CoCeO$_2$ catalysts with Co loading of (b) 1.06 *wt*.%, (c) 2.45 *wt*.% and (d) 4.32 *wt*.%, respectively.
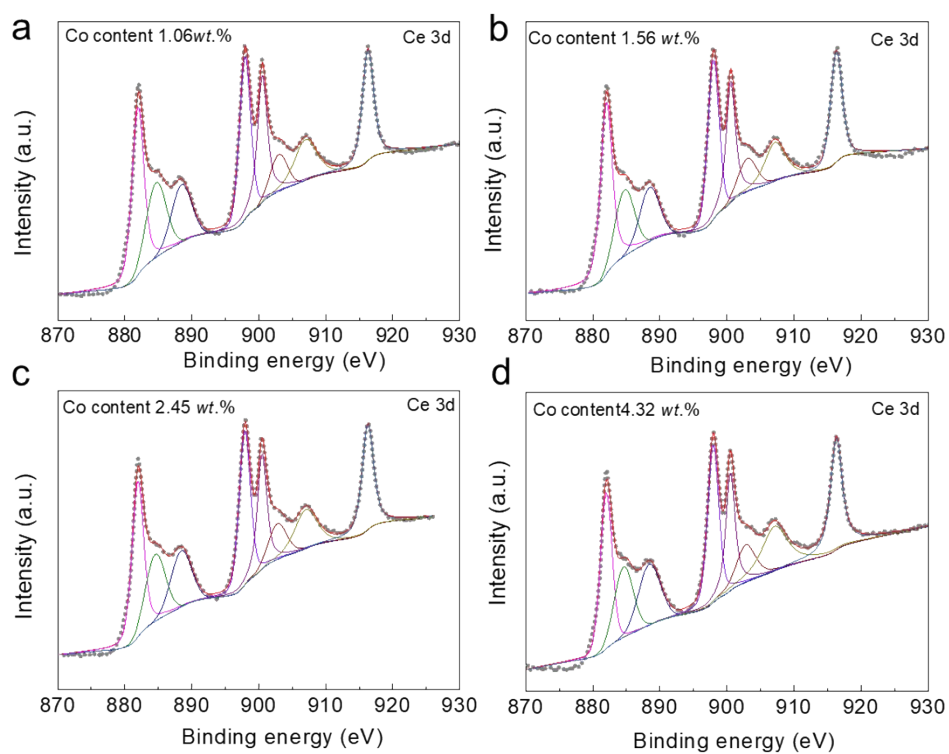
Figure S11. XPS analysis of Ce *3d* for the NR-CoCeO$_2$ catalysts with Co loading of (a)

1.06 *wt.%*, (b) 1.56 *wt.%*, (c) 2.45 *wt.%* and (d) 4.32 *wt.%*, respectively.
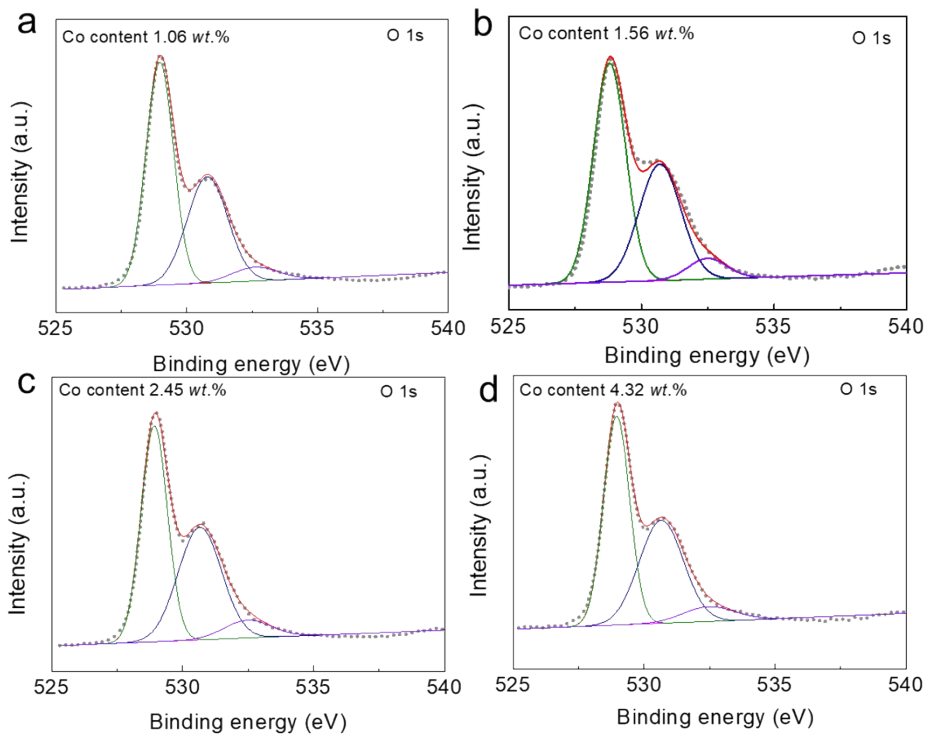
Figure S12. XPS analysis of O *1s* for the NR-CoCeO$_2$ catalysts with Co loading of (a) 1.06 *wt*.%, (b) 1.56 *wt*.%, (c) 2.45 *wt*.% and (d) 4.32 *wt*.%, respectively.
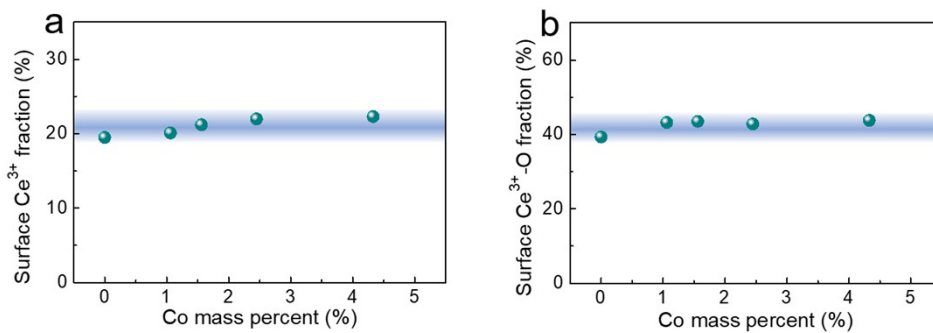

Figure S13. The influence of Co precents on the surface (a) Ce^{3+} and (b) Ce^{3+}-O fraction of the NR-CoCeO$_2$ catalysts.
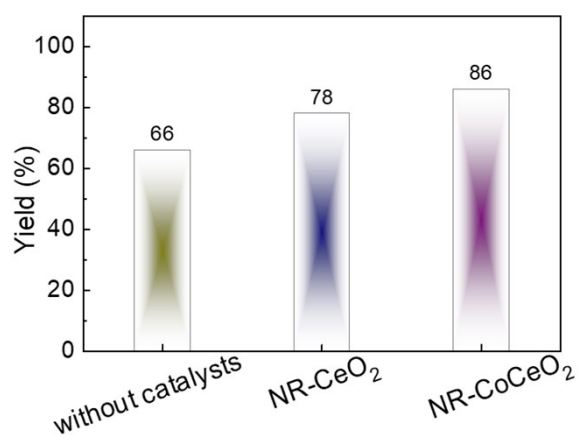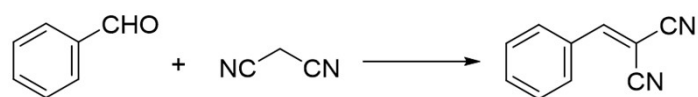
Figure S14. Catalytic preformation of various catalysts for the condensation of benzaldehyde and malononitrile into benzylidenemalononitrile. **Reaction conditions**: benzaldehyde (2 mL), malononitrile (0.5 mmol), catalysts (5 mg), 2 h and 60 °C.