# Electronic supplementary information

## Growth of $LaCoO_3$ crystals in molten salt: Effects of synthesis conditions

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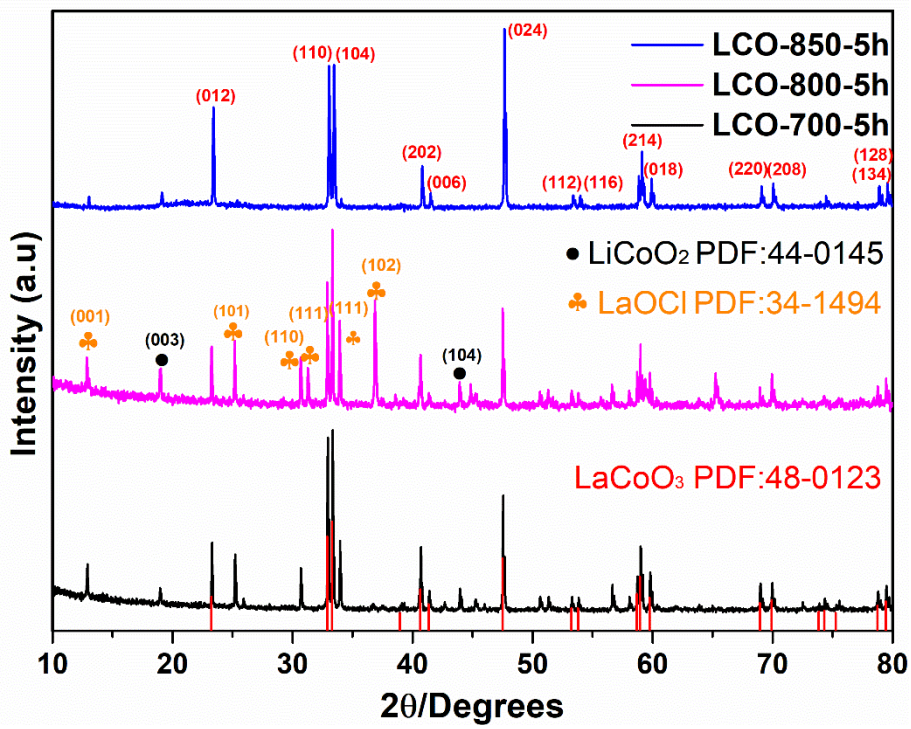



**Fig. S1** XRD patterns of samples obtained at different temperature for 5 h with LiCl-KCl molten salts.

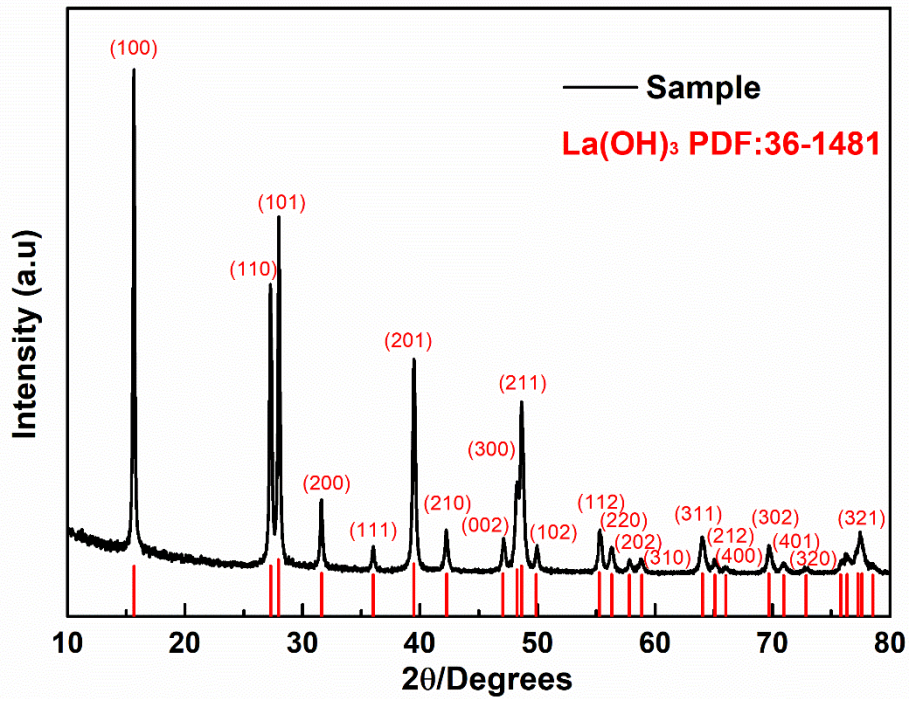



**Fig. S2** XRD patterns of the sample obtained after the $La_2O_3$ soaked into the $Na_2CO_3$-$K_2CO_3$ eutectic salt at 850 °C for 5 h.

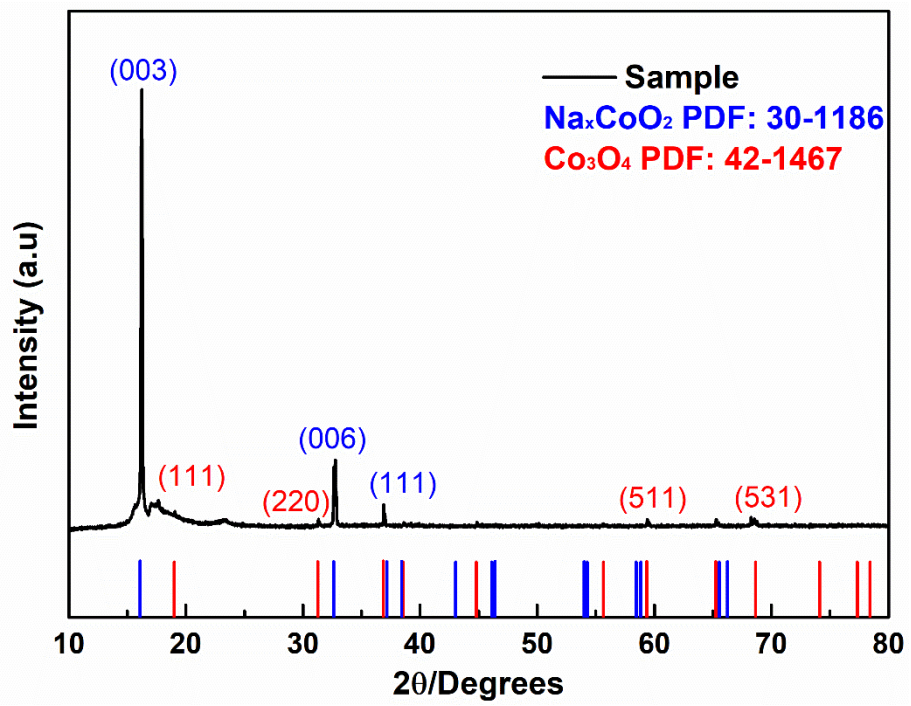



**Fig. S3** XRD patterns of the sample obtained after $Co_3O_4$ soaked into the $Na_2CO_3$-$K_2CO_3$ eutectic salts at 850 °C for 5 h.

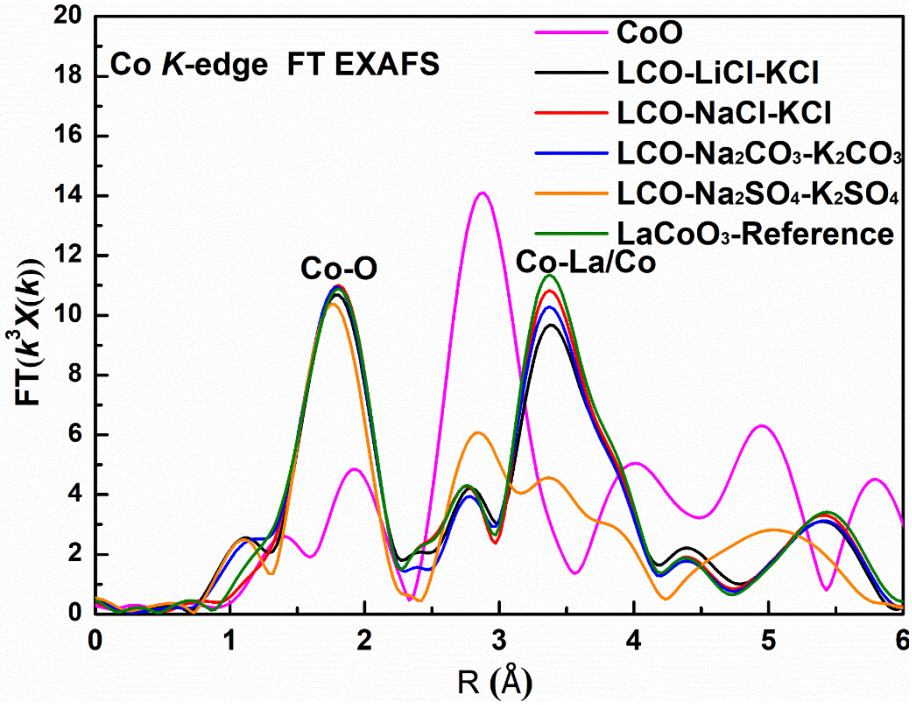



**Fig. S4** Fourier transform (FT) of the Co K-edge EXAFS of synthesized samples and references.

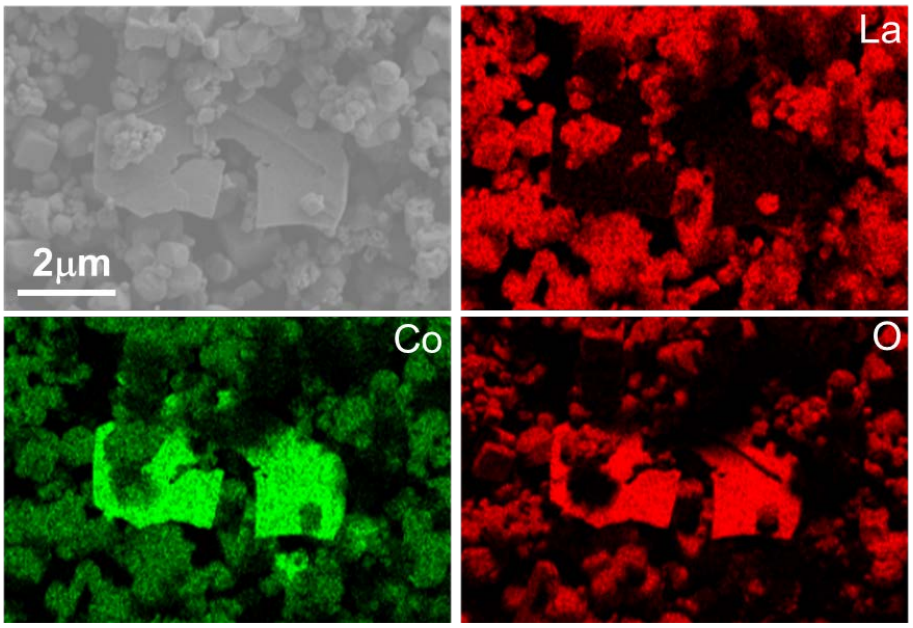
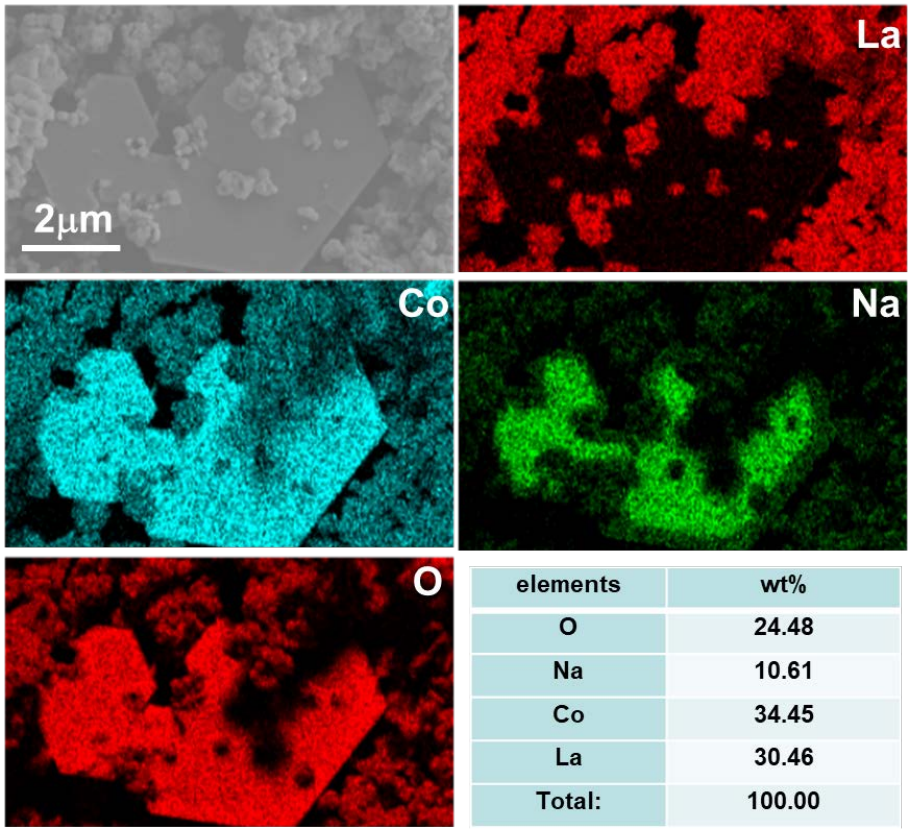



**Fig. S5** SEM image and corresponding elemental mapping images of the synthesized sample in the LiCl-KCl eutectic salt at 850 °C for 5 h.




| elements | wt% |
|---|---|
| O | 24.48 |
| Na | 10.61 |
| Co | 34.45 |
| La | 30.46 |
| Total: | 100.00 |

**Fig. S6** SEM image and corresponding elemental mapping images of the synthesized sample in the $Na_2CO_3$-$K_2CO_3$ eutectic salt at 850 °C for 5 h.

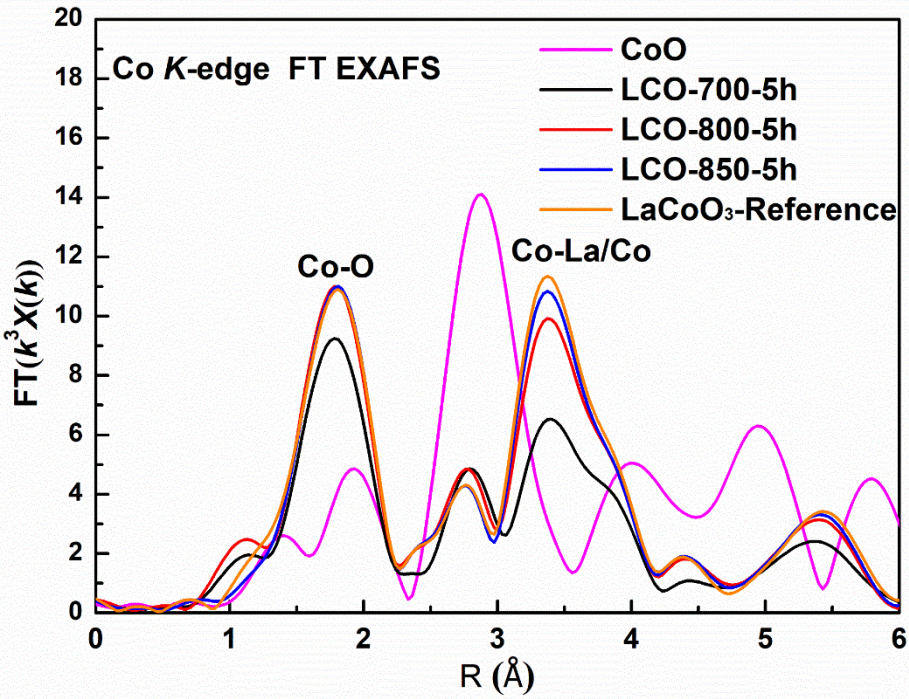



**Fig. S7** Fourier transform (FT) of the Co K-edge EXAFS of synthesized samples under different temperatures and references.

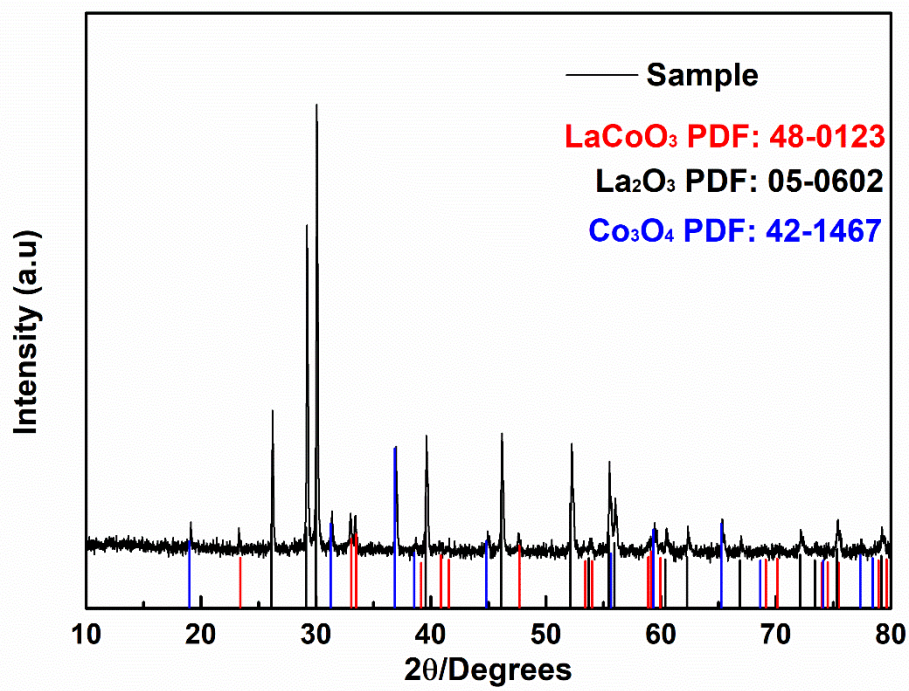



**Fig. S8** XRD patterns of samples obtained by solid state method at 700 °C for 10 h.

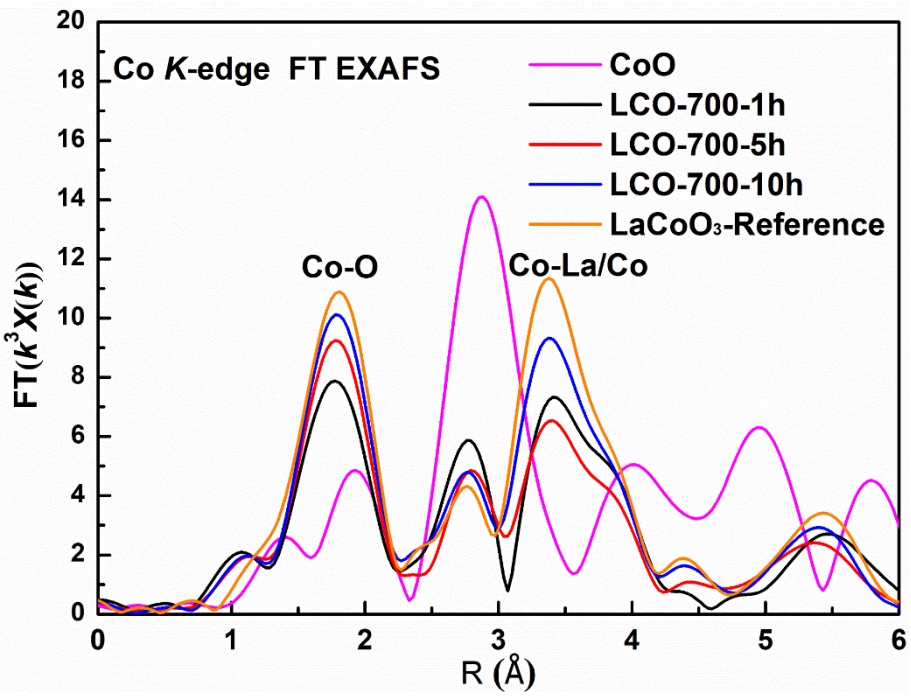



**Fig. S9** Fourier transform (FT) of the Co K-edge EXAFS of the samples synthesized at 700 °C with different times and references.

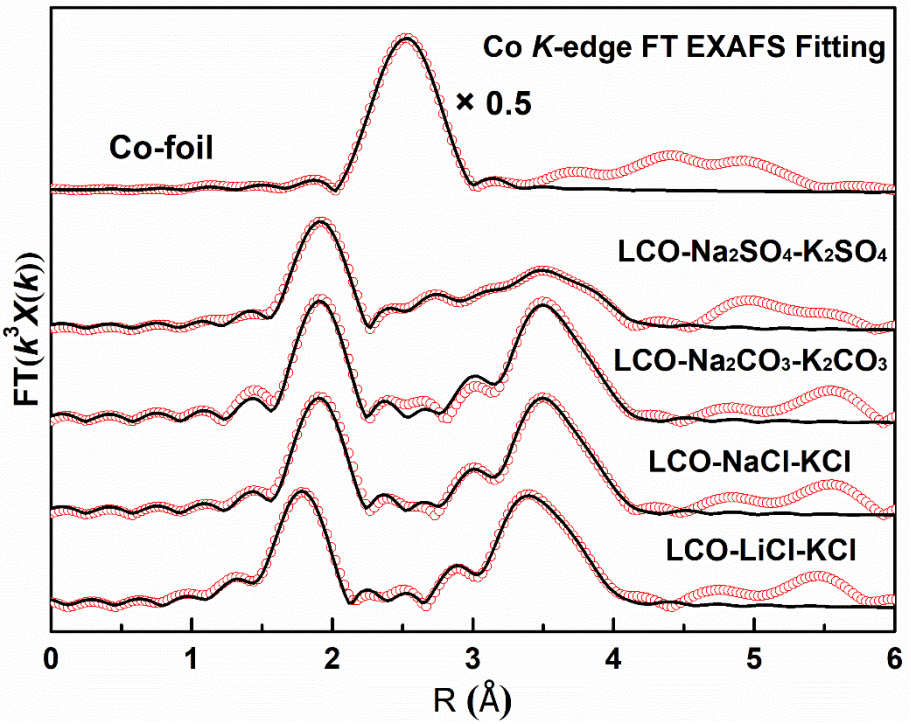



**Fig. S10** EXAFS fitting curves for LCO with different molten salts. (FT range: 2.5 - 12.0 $Å^{-1}$).

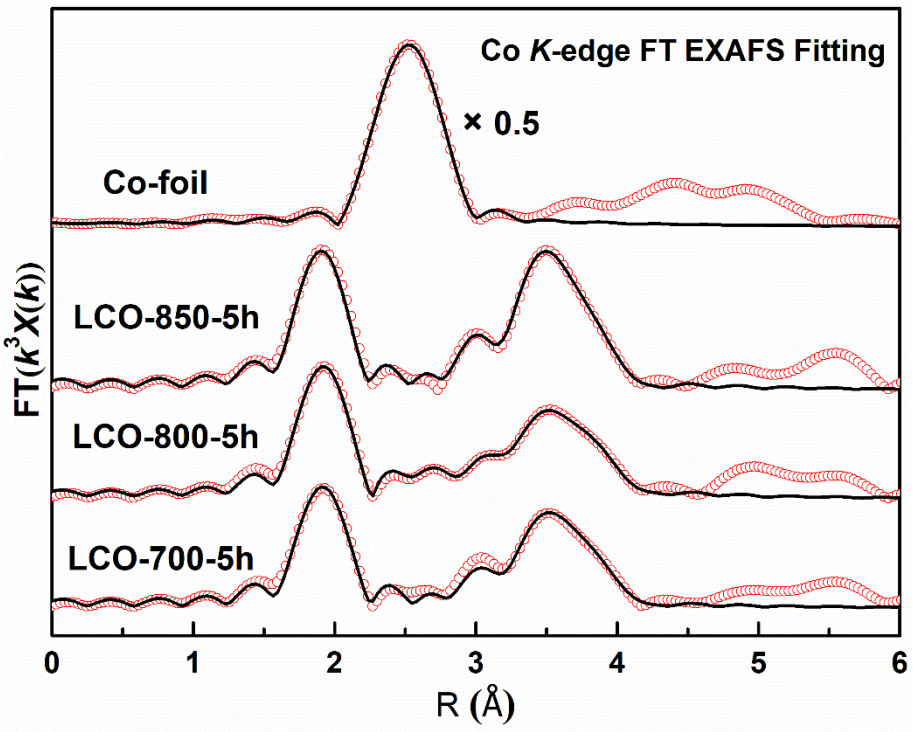



**Fig. S11** EXAFS fitting curves for LCO with different temperature for 5 h. (FT range: 2.5 - 12.0 $Å^{-1}$).

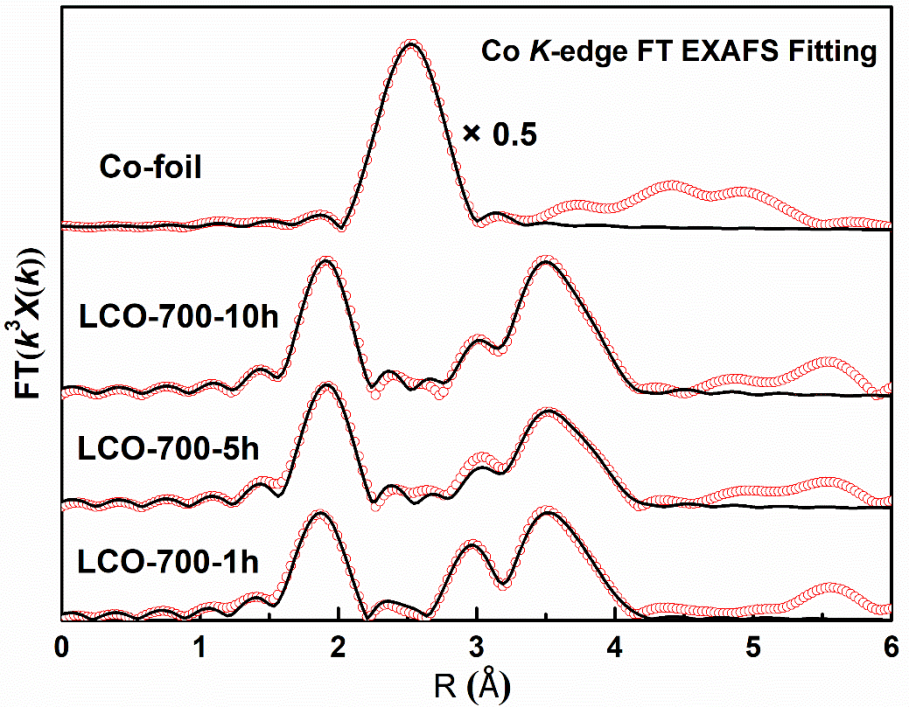



**Fig. S12** EXAFS fitting curves for LCO at 700 °C with different time. (FT range: 2.5 - 12.0 $Å^{-1}$).

**Table S1** melting points and composition of some used metal salt systems.

| Salt system | Composition (mol %) | Melting point (°C) |
|---|---|---|
| NaCl | 100 | 801 |
| KCl | 100 | 771 |
| LiCl-KCl | 59 / 41 | 353 |
| NaCl- KCl | 50 / 50 | 657 |

| | | |
|---|---|---|
| $NaCl$-$Na_2CO_3$ | 55 / 45 | 632 |
| $NaCl$-$Na_2SO_4$ | 53 / 47 | 617 |
| $KCl$-$K_2CO_3$ | 62 / 38 | 631 |
| $KCl$- $K_2SO_4$ | 74 / 26 | 690 |
| $Na_2CO_3$-$K_2CO_3$ | 58 / 42 | 709 |
| $Na_2SO_4$-$K_2SO_4$ | 74 / 26 | 834 |

**Table S2** Firing conditions and batch compositions of samples.

| **Samples No.** | **Firing conditions** | **Salt assembly (molar ratios)** | **Reactant: salt ratio (wt.) %** |
|---|---|---|---|
| S0 | 850 °C / 5 h | LiCl-KCl (0.55:0.45) | 1:2 |
| S1 | | $Na_2SO_4$-$K_2SO_4$ (0.74:0.26) | |
| S2 | | $Na_2CO_3$-$K_2CO_3$ (0.58:0.42) | |
| S3 | | $NaCl$-$Na_2CO_3$ (0.55:0.45) | |
| S4 | | $NaCl$-$Na_2SO_4$ (0.50:0.50) | |
| S5 | | $KCl$-$K_2CO_3$ (0.60:0.40) | |
| S6 | | $KCl$- $K_2SO_4$ (0.75:0.25) | |
| S7 | | KCl | |
| S8 | | NaCl | |
| T1 | 800 °C / 5 h | NaCl-KCl (0.50:0.50) | |
| T2 | 700 °C / 10 h | | |
| T3 | 700 °C / 5 h | | |
| T4 | 700 °C / 1 h | | |
| K1 | 700 °C / 10 h | No salt | |
| K2 | 700 °C / 10 h | NaCl-KCl (0.50:0.50) | 1:5 |
| K3 | 700 °C / 10 h | NaCl-KCl (0.50:0.50) | 1:10 |

**Table S3** Structural parameters of Co foil and samples synthesized via different molten salts at 850 °C, for 5 h.

| Sample | Atomic Scatter | Coordination Number | Bond Length (Å) | Debye-Waller factor ($10^{-3}$×Å$^2$) | R factor |
|---|---|---|---|---|---|
| Co -foil | Co-Co | 12 | 2.49 ± 0.01 | 6.2 ± 0.2 | 0.001 |
| LCO-NaCl-KCl | Co-O | 5.5 ± 0.3 | 1.92 ± 0.01 | 3.3 ±0.2 | 0.007 |
| | Co-La | 6.1 ± 0.2 | 3.33 ± 0.01 | 4.6 ±0.3 | |
| | Co-Co | 3.0 ± 0.4 | 3.89 ± 0.01 | 1.7 ±0.4 | |
| LCO-LiCl-KCl | Co-O | 5.6 ± 0.2 | 1.92 ± 0.01 | 3.3 ± 0.3 | 0.004 |
| | Co-La | 5.9 ± 0.2 | 3.33 ± 0.01 | 4.5 ± 0.2 | |
| | Co-Co | 3.3 ± 0.4 | 3.89 ± 0.01 | 2.0 ± 0.5 | |

| | | | | | |
|---|---|---|---|---|---|
| LCO-$Na_2CO_3$-$K_2CO_3$ | Co-O | 5.4 ± 0.3 | 1.92 ± 0.01 | 2.6 ± 0.6 | 0.014 |
| | Co-La | 6.3 ± 0.5 | 3.33 ± 0.01 | 4.7 ± 0.5 | |
| | Co-Co | 3.2 ± 0.6 | 3.89 ± 0.01 | 2.1 ± 1.0 | |
| LCO-$Na_2SO_4$-$K_2SO_4$ | Co-O | 4.9 ± 0.2 | 1.92 ± 0.01 | 2.5 ± 0.4 | 0.005 |
| | Co-La | 2.9 ± 0.4 | 3.36 ± 0.01 | 3.2 ± 0.8 | |
| | Co-Co | 2.6 ± 0.5 | 3.87 ± 0.01 | 3.4 ± 1.2 | |
| | Co-Co'' | 3.1 ± 0.9 | 2.89 ± 0.01 | 6.7 ± 1.5 | |

**Table S4** Structural parameters of Co foil and abstained products under different temperatures for 5 h extracted from the Co K-edge EXAFS fitting.

| Sample | Atomic Scatter | Coordination Number | Bond Length (Å) | Debye-Waller factor ($10^{-3}$×Å$^2$) | R factor |
|---|---|---|---|---|---|
| Co -foil | Co-Co | 12 | 2.49 ± 0.01 | 6.2 ± 0.2 | 0.001 |
| LCO-700-5h | Co-O | 4.5 ± 0.4 | 1.93 ± 0.01 | 2.5 ± 0.7 | 0.028 |
| | Co-La | 3.7 ± 0.5 | 3.34 ± 0.01 | 3.8 ± 0.7 | |
| | Co-Co | 2.3 ± 0.7 | 3.90 ± 0.01 | 1.8 ± 1.2 | |
| LCO-800-5h | Co-O | 4.9 ± 0.2 | 1.92 ± 0.01 | 2.4 ± 0.4 | 0.007 |
| | Co-La | 3.5 ± 0.4 | 3.33 ± 0.01 | 3.7 ± 0.4 | |
| | Co-Co | 3.0 ± 0.5 | 3.89 ± 0.01 | 3.3 ± 0.9 | |
| LCO-850-5h | Co-O | 5.3 ± 0.2 | 1.93 ± 0.01 | 2.2 ± 0.4 | 0.004 |
| | Co-La | 3.7± 0.3 | 3.35 ± 0.01 | 3.4 ± 0.4 | |
| | Co-Co | 3.0 ± 0.5 | 3.89 ± 0.01 | 1.7 ± 0.7 | |

**Table S5** Structural parameters of Co foil and synthesized samples under 700 °C with different times extracted from the Co K-edge EXAFS fitting.

| Sample | Atomic Scatter | Coordination Number | Bond Length (Å) | Debye-Waller factor ($10^{-3}$×Å$^2$) | R factor |
|---|---|---|---|---|---|
| Co -foil | Co-Co | 12 | 2.49 ± 0.01 | 6.2 ± 0.2 | 0.001 |
| LCO-700-1h | Co-O | 4.0 ± 0.2 | 1.92 ± 0.01 | 2.6 ± 0.5 | 0.004 |
| | Co-La | 3.8 ± 0.3 | 3.32 ± 0.01 | 3.3 ± 0.4 | |
| | Co-Co | 2.8 ± 0.5 | 3.91 ± 0.01 | 1.9 ± 0.9 | |
| | Co-Co' | 6.0 ± 0.4 | 3.02 ± 0.01 | 14.5 ± 0.9 | |
| | Co-O | 4.5 ± 0.4 | 1.93 ± 0.01 | 2.5 ± 0.6 | 0.028 |

| | | | | | |
|---|---|---|---|---|---|
| LCO-700-5h | Co-La | 3.7 ± 0.5 | 3.34 ± 0.01 | 3.8 ± 0.2 | |
| | Co-Co | 2.3 ± 0.7 | 3.90 ± 0.01 | 1.8 ± 0.9 | |
| LCO-700-10h | Co-O | 5.6 ± 0.3 | 1.92 ± 0.01 | 3.5 ± 0.5 | 0.009 |
| | Co-La | 5.5 ± 0.3 | 3.33 ± 0.01 | 4.1 ± 0.3 | |
| | Co-Co | 3.6 ± 0.6 | 3.88 ± 0.01 | 3.0 ± 0.9 | |