**Supplementary material for**

**Hierarchical cobalt-nitride and -oxide co-doped porous carbon nanostructures for highly efficient and durable bifunctional oxygen reaction electrocatalysts**

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This document includes Supplementary figures (Figure S1-S15) and tables (Table S1-S3).
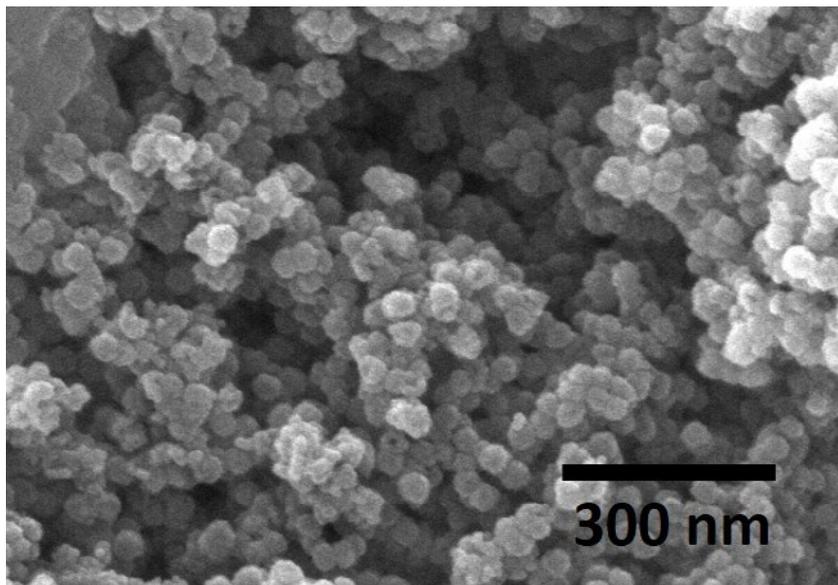
**Figure S1**. SEM image of hollow N-doped carbon microspheres.
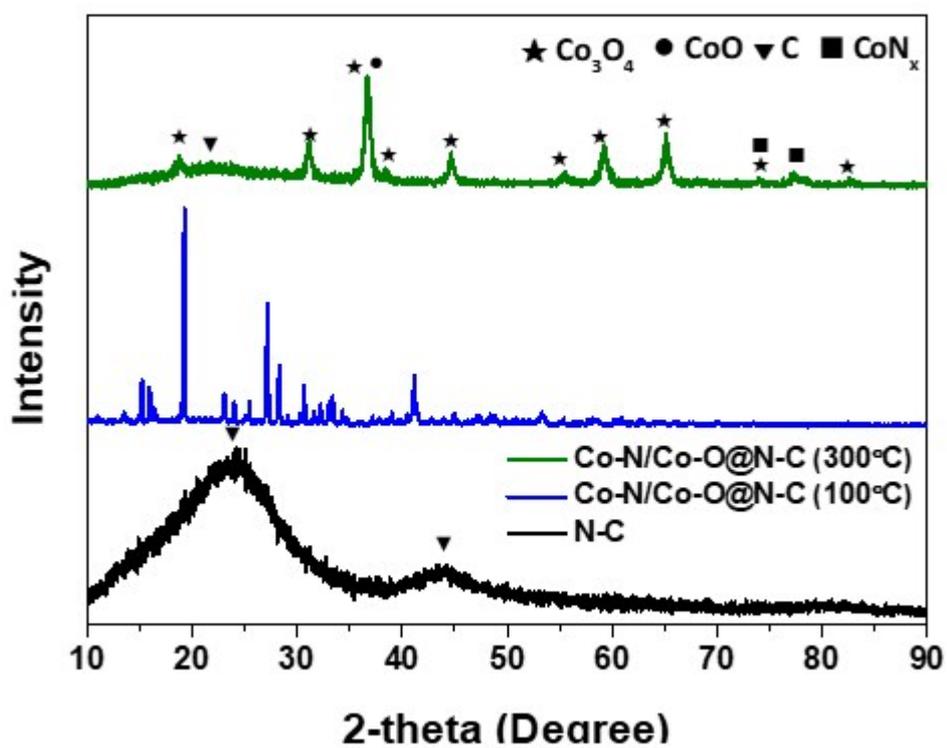
**Figure S2**. XRD patterns of hollow N-C and Co-N/Co-O@N-C (100°C) and Co-N/Co-O@N-C (300 °C). All peaks of Co-N/Co-O@N-C (100°C) indicated cobalt nitrate hydrate $(Co(NO_3)_2 6H_2O)$. (JCPDS#25-1219)
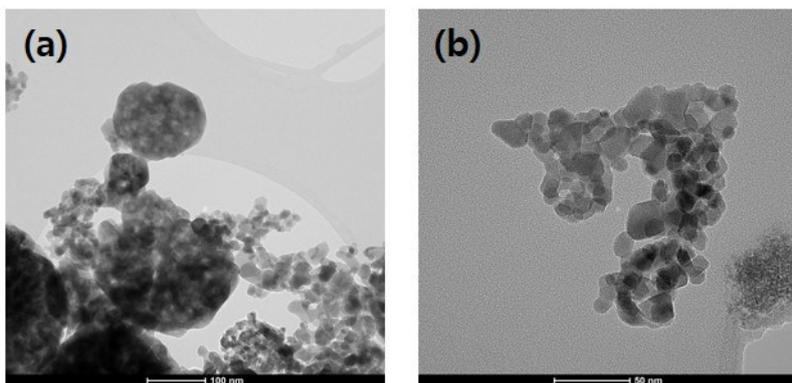
**Figure S3**. TEM images of Co-N/Co-O@N-C samples treated with $Co(NO_3)_2 \cdot 6H_2O$ of 5M concentration (a) and annealed at 400°C (b).
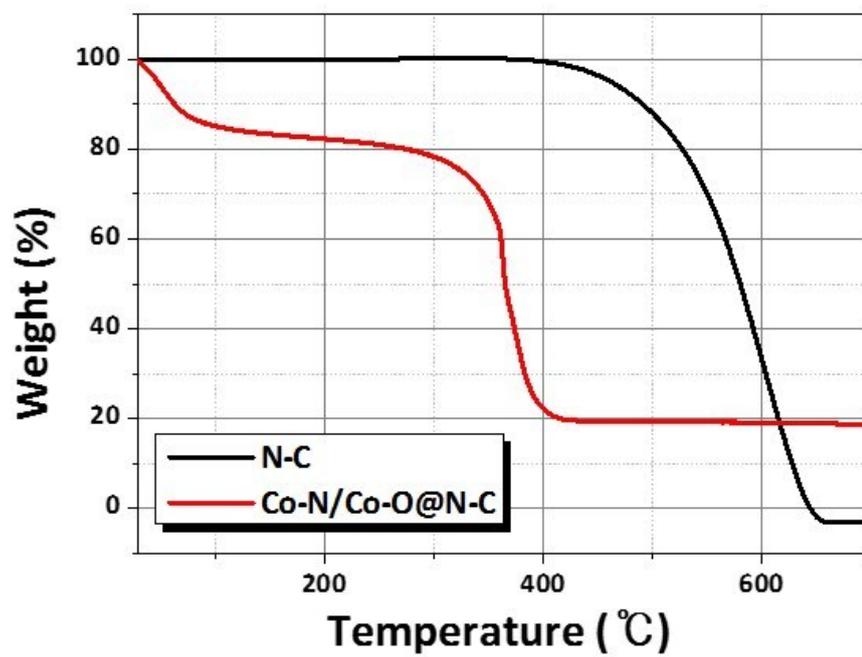
**Figure S4**. TGA profiles of hollow N-C and Co-N/Co-O@N-C samples.
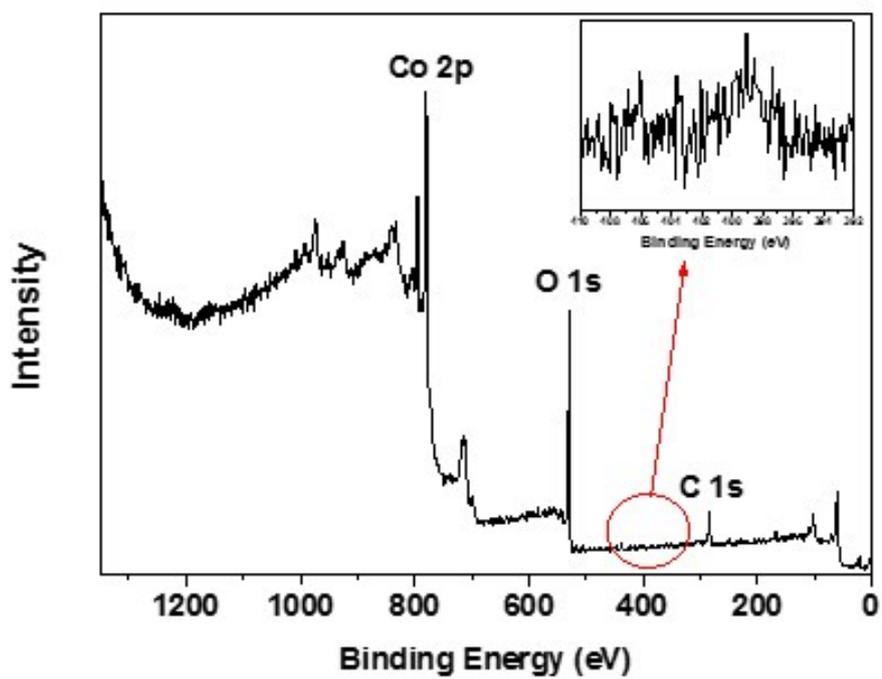
**Figure S5**. XPS survey spectrum of Co-N/Co-O@N-C (400°C) and N1s narrow-scan spectrum in inner box.
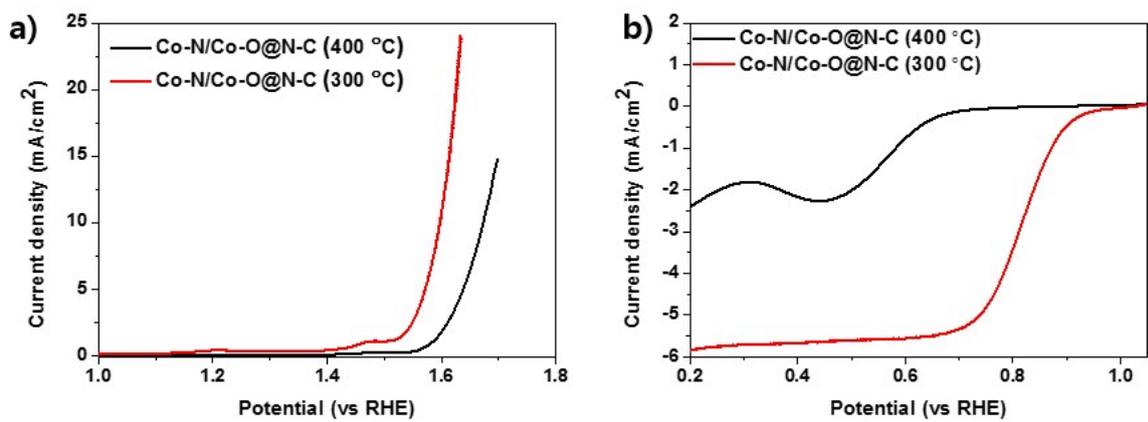
**Figure S6**. Electrochemical measurements of the Co-N/Co-O@N-C samples heat-treated at 300°C and 400°C: (a) OER polarization curves and (b) ORR polarization curves.
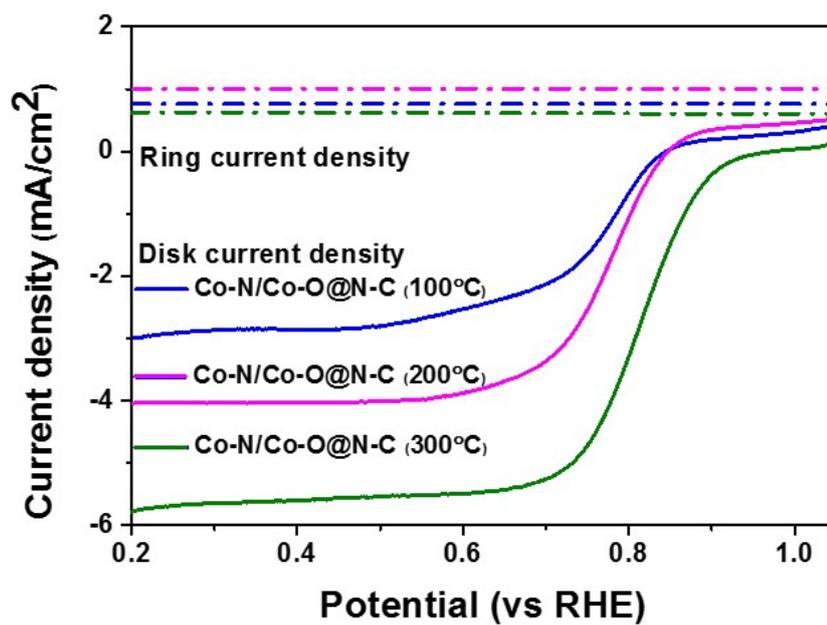
**Figure S7**. RRDE test of the ORR on Co-N/Co-O@N-C according to the annealing temperature in $O_2$-satruraed 0.1M KOH aqueous solution at 1600 rpm.
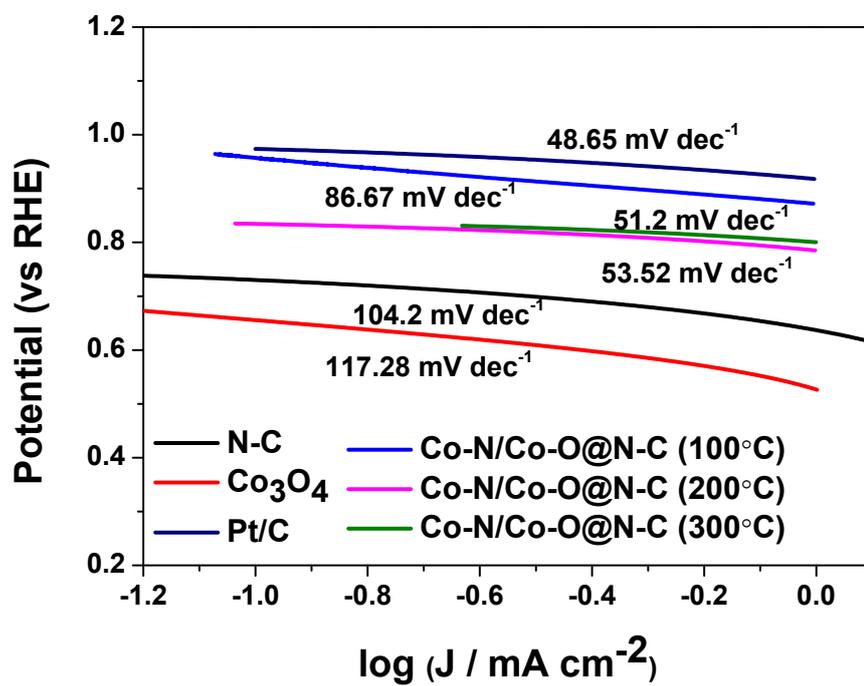
**Figure S8**. ORR Tafel plot.
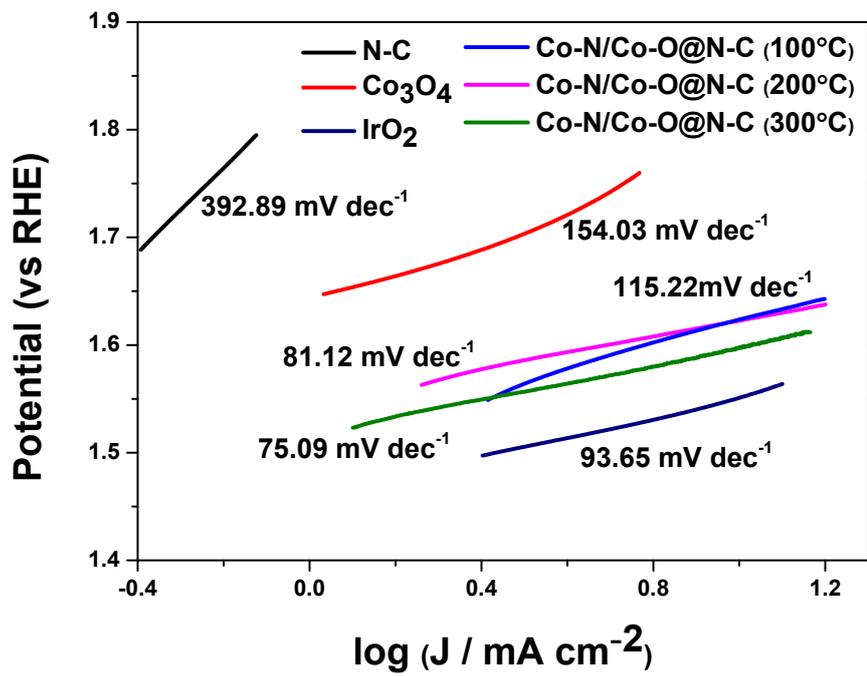
**Figure S9**. OER Tafel plot.
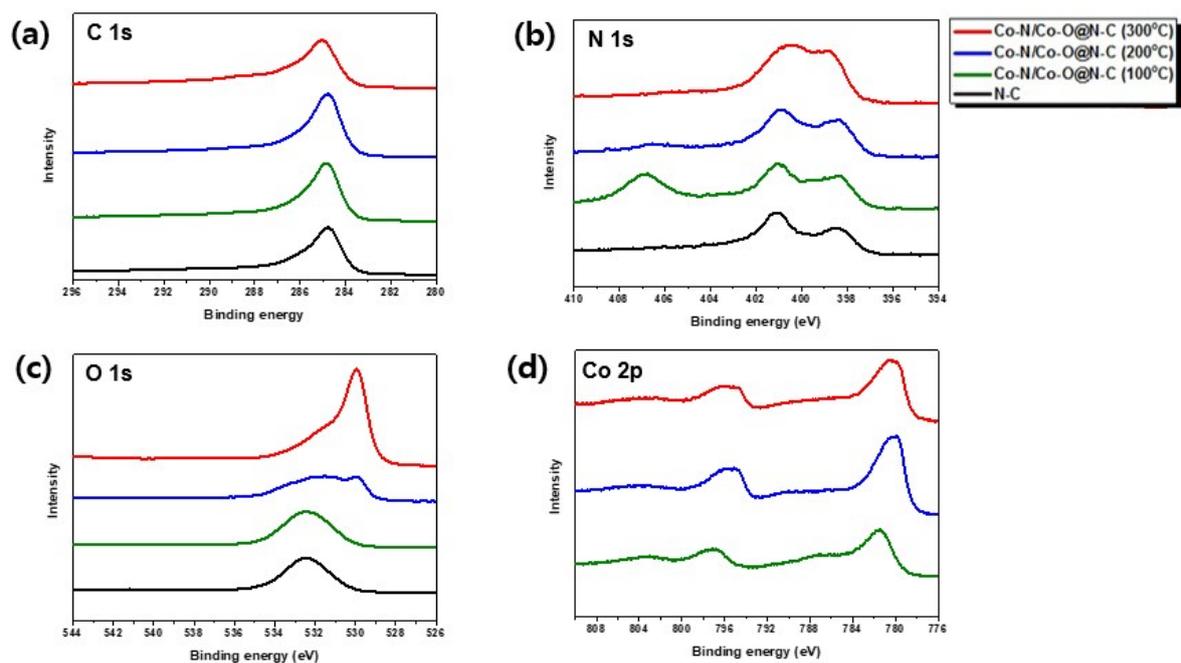
**Figure S10**. XPS spectra of the samples for N-C and Co-N/Co-O@N-C samples annealed at 100, 200 and 300°C: (a) C1s, (b) N1s, (c) O1s and (d) Co2p.
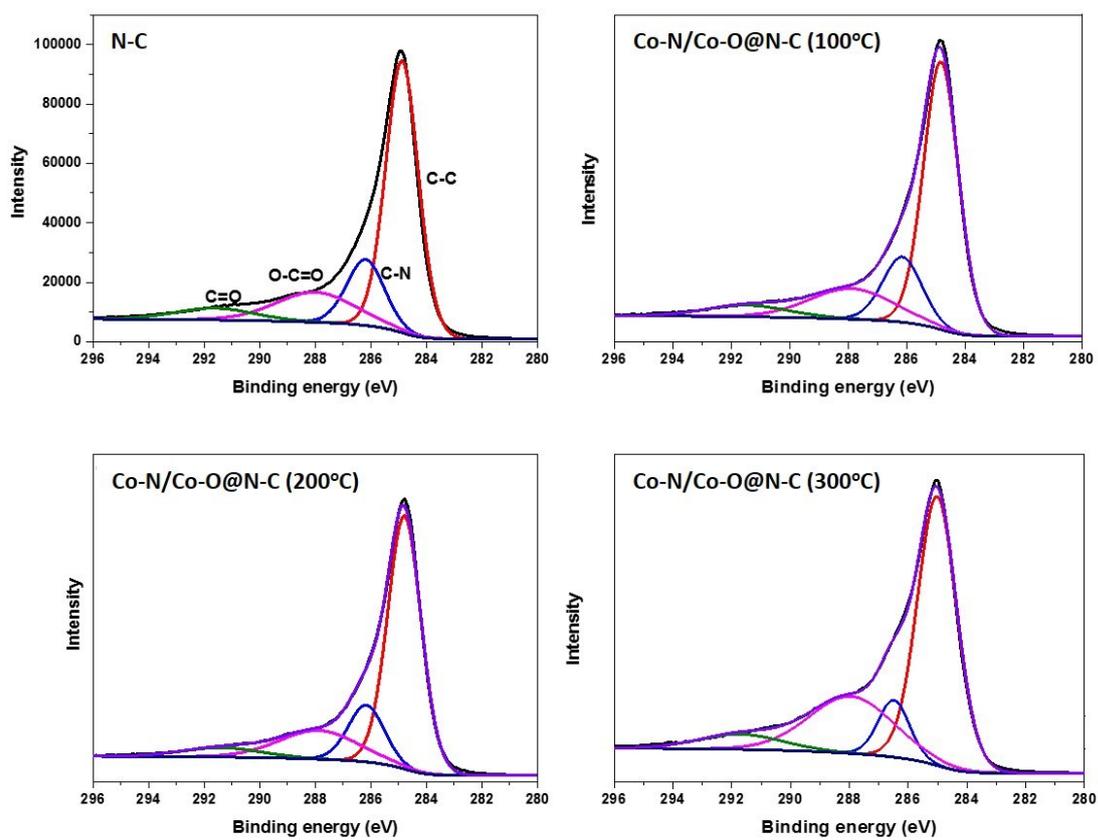
**Figure S11**. Deconvolution of XPS C1s spectra of the samples for N-C and Co-N/Co-O@N-C samples annealed at 100, 200 and 300°C.
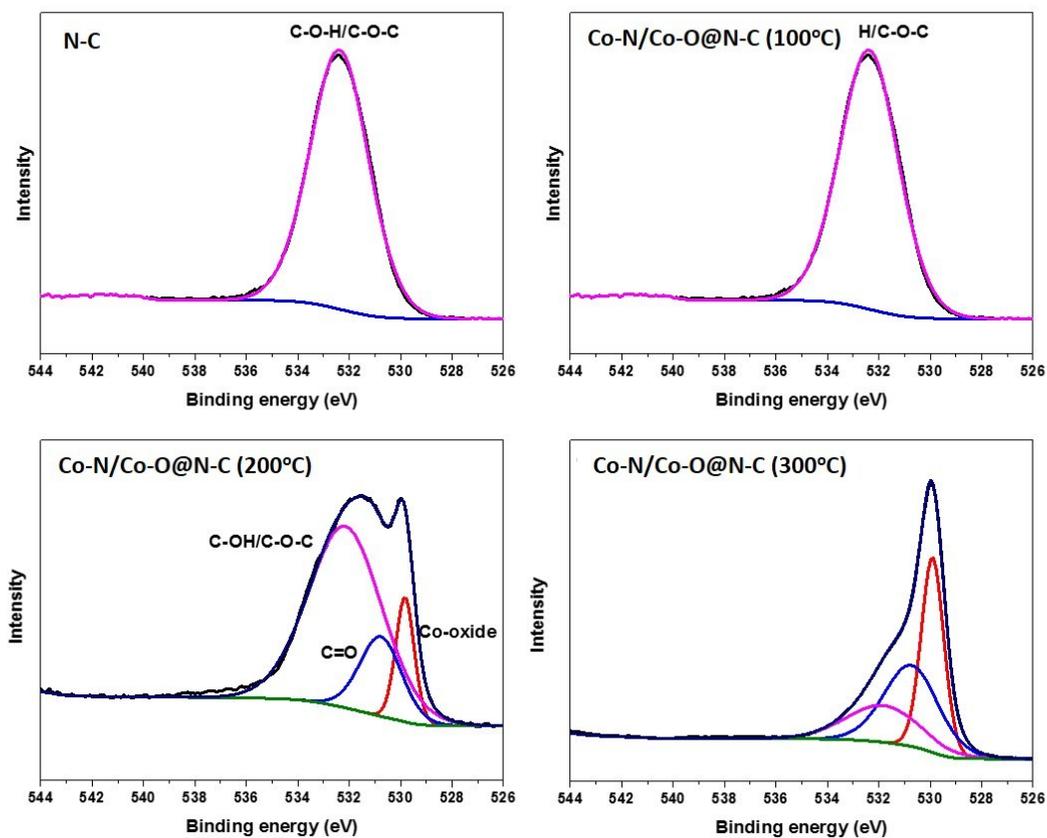
**Figure S12**. Deconvolution of XPS O1s spectra of the samples for N-C and Co-N/Co-O@N-C samples annealed at 100, 200 and 300°C.
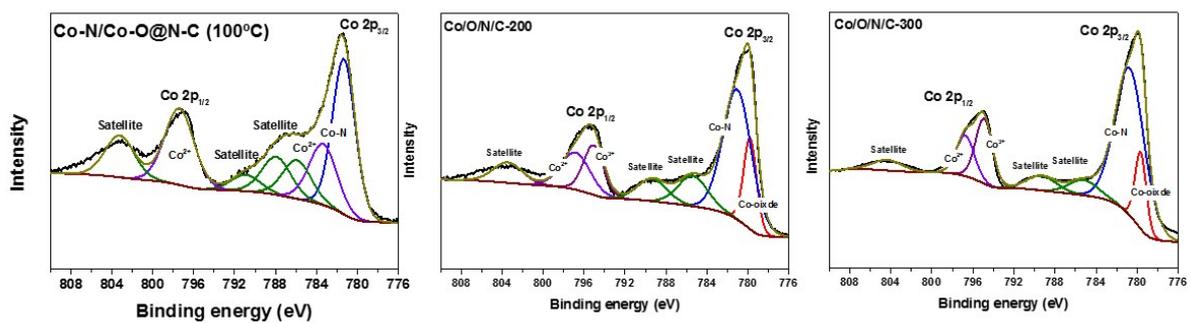
**Figure S13**. Deconvolution of XPS Co2p spectra of the samples for Co-N/Co-O@N-C samples annealed at 100, 200 and 300°C.
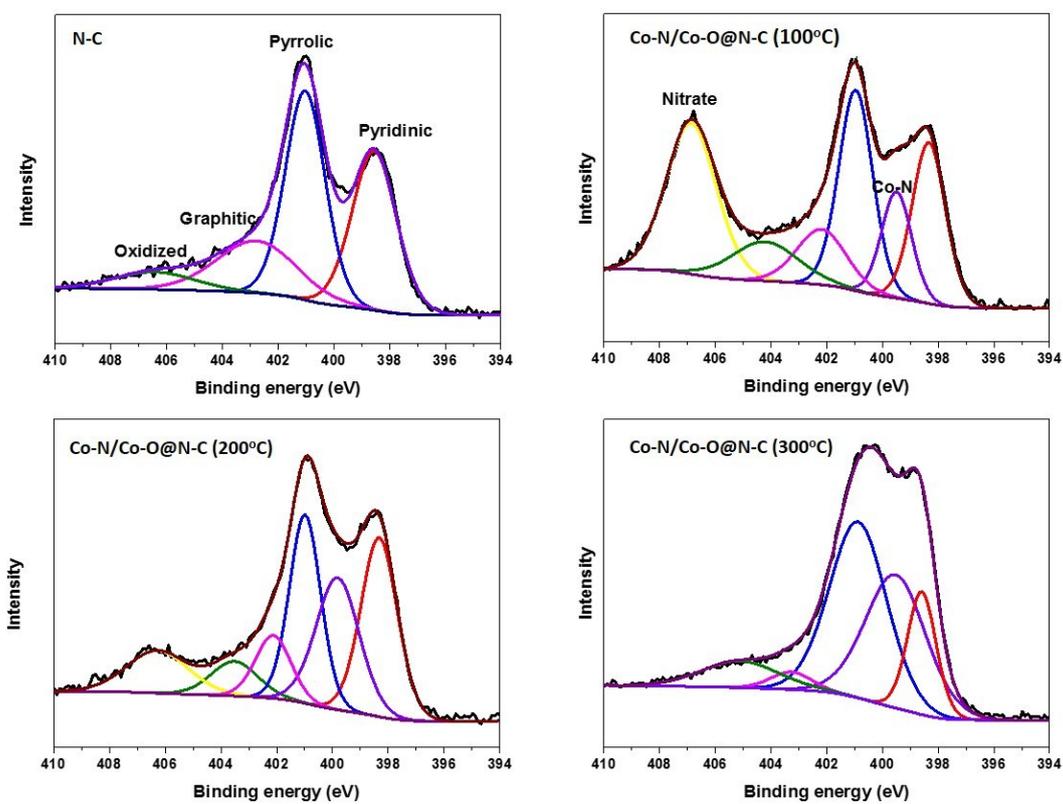
**Figure S14**. Deconvolution of XPS N1s spectra of the samples for N-C and Co-N/Co-O@N-C samples annealed at 100, 200 and 300°C.
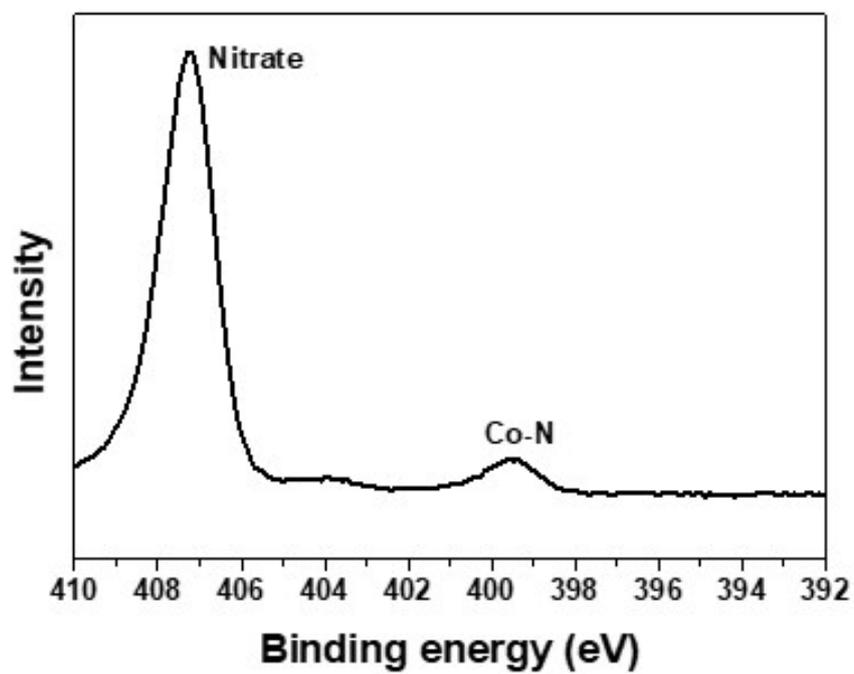
**Figure S15**. N 1s narrow-scan spectrum of Co-N/Co-O@N-C phase prepared via heat-treatment (~100°C) of cobalt nitrate with hollow N-doped carbon microsphere.

| Sample | Specific surface area | Total pore volume | Average pore size |
|---|---|---|---|
| N-C | 846 m$^2$/g | 0.306 cm$^3$/g | 9.44 nm |
| Co-N/Co-O@N-C | 493 m$^2$/g | 0.186 cm$^3$/g | 8.23 nm |

**Table S1**. Specific surface area, total pore volume, average pore size from N$_2$ adsorption-desorption isotherms of hollow N-C and Co-N/Co-O@N-C samples.

| Sample | Specific surface area | Total pore volume | Average pore size |
|---|---|---|---|
| Co-N/Co-O@N-C (400°C) | 25.34 m$^2$/g | 0.119 cm$^3$/g | 18.9 nm |

**Table S2**. Specific surface area, total pore volume, average pore size from N$_2$ adsorption-desorption isotherms of Co-N/Co-O@N-C (400°C) sample.

| Co(K)-N | Coordination number |
|---|---|
| Co-N/Co-O@N-C (100°C) | 0.452 |
| Co-N/Co-O@N-C (200°C) | 1.198 |
| Co-N/Co-O@N-C (300°C) | 1.155 |

**Table S3**. Coordination numbers of cobalt attached to nitrogen in Co-N/Co-O@N-C complexes.