# Supplementary Information

**MOF derived Porous N-$Co_3O_4$@N-C Nanopolyhedra Wrapped With Reduced Graphene Oxide as High Capacity Cathodes for Lithium-Sulfur Batteries**

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KEYWORDS: Metal–Organic-Framework; Cobalt oxide; Cathode material; Lithium-sulfur batteries

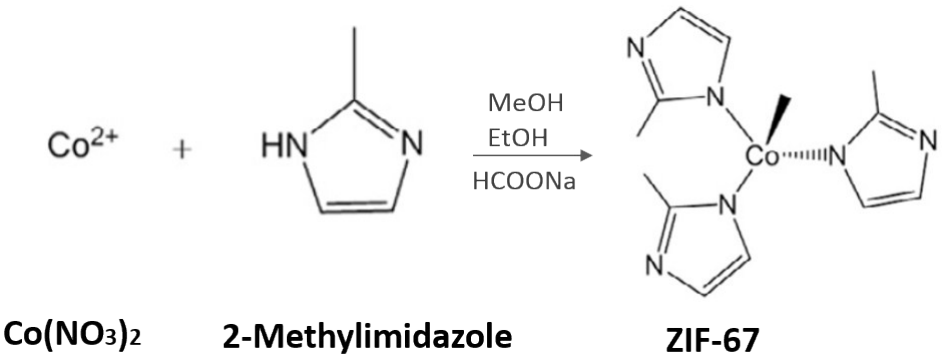


**Figure S1** Chemical equation for the synthesis of ZIF-67.

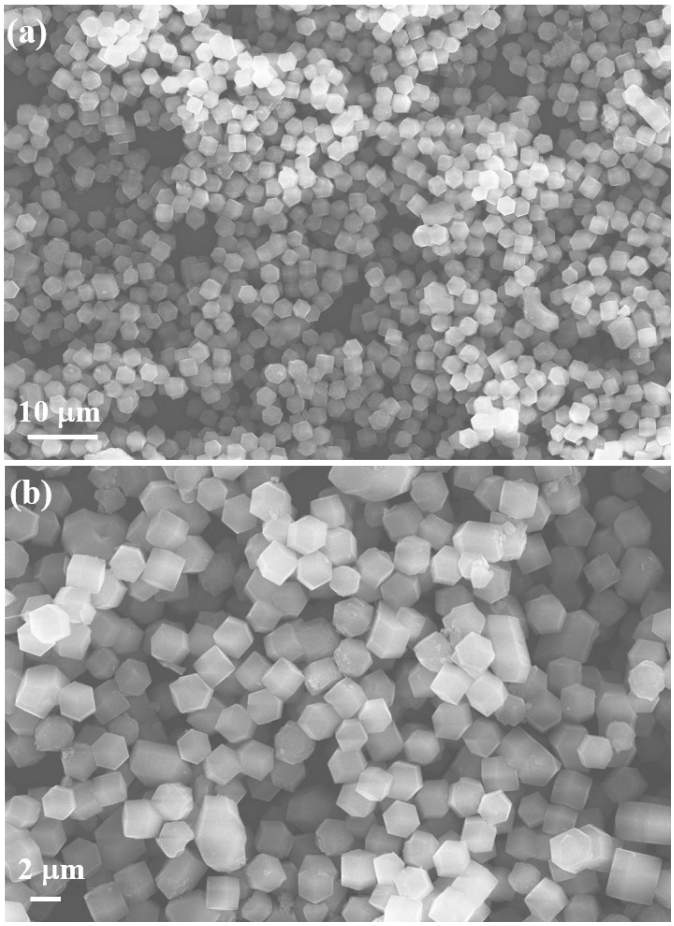


**Figure S2** (a, b) SEM image of ZIF-67

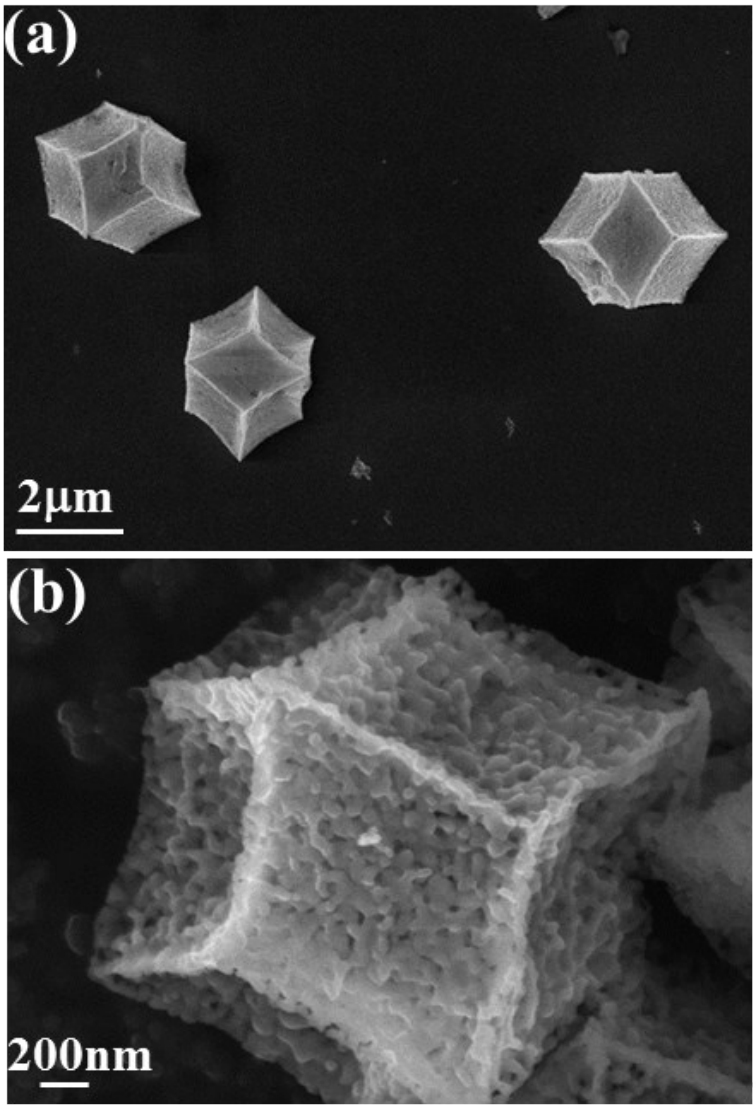


**Figure S3** SEM images of (a, b) N-$Co_3O_4$@N-C.

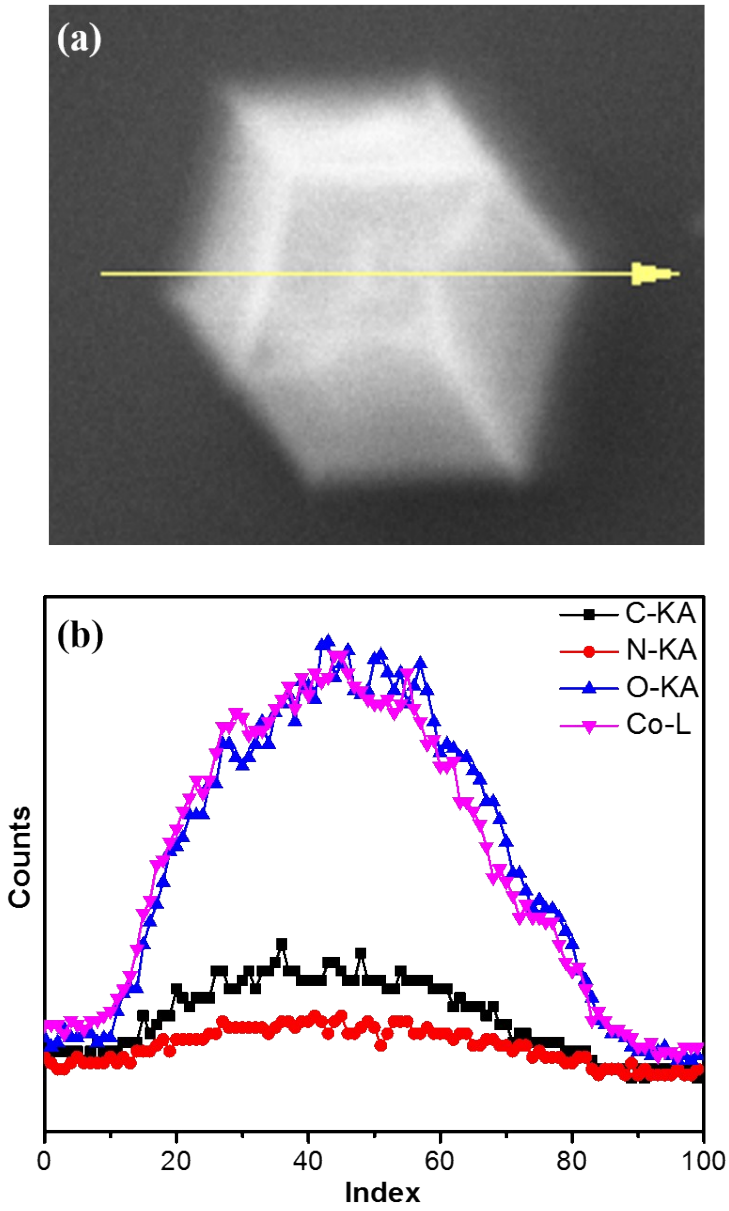


**Figure S4** Linear distributions of C, N, O and Co along the arrow line on the inset image of N-$Co_3O_4$@N-C.

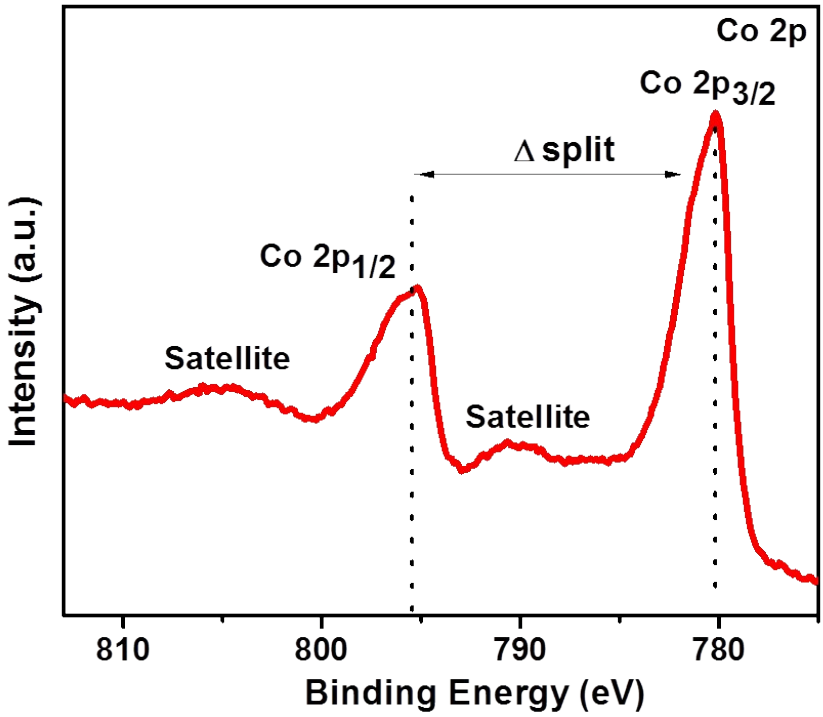


**Figure S5** Co 2p spectrum of the N-$Co_3O_4$@N-C composite.

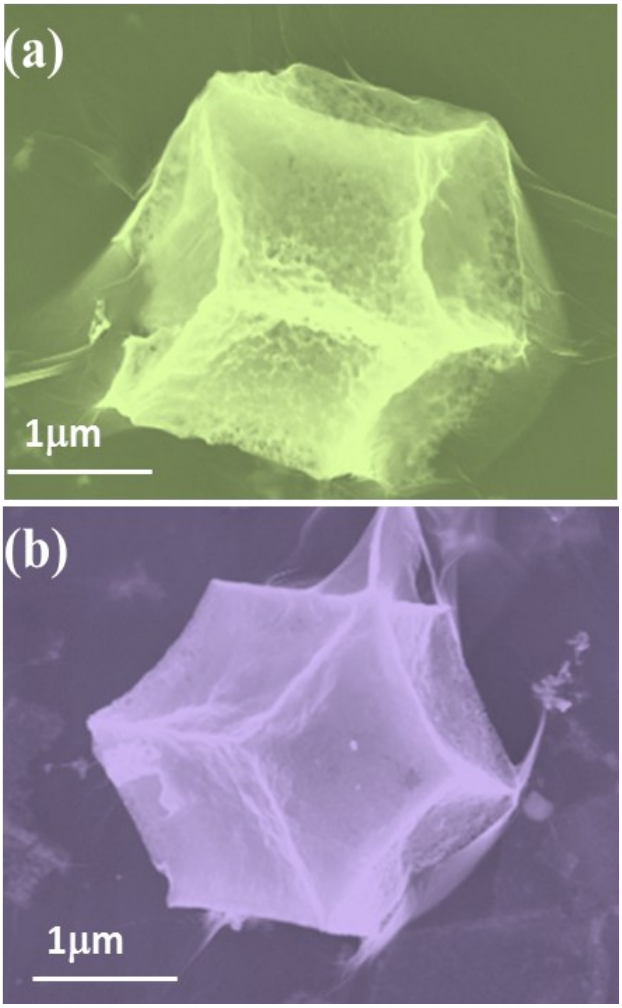


**Figure S6** SEM images of (a) N-$Co_3O_4$@N-C/GO and (b) N-$Co_3O_4$@N-C/rGO-S.

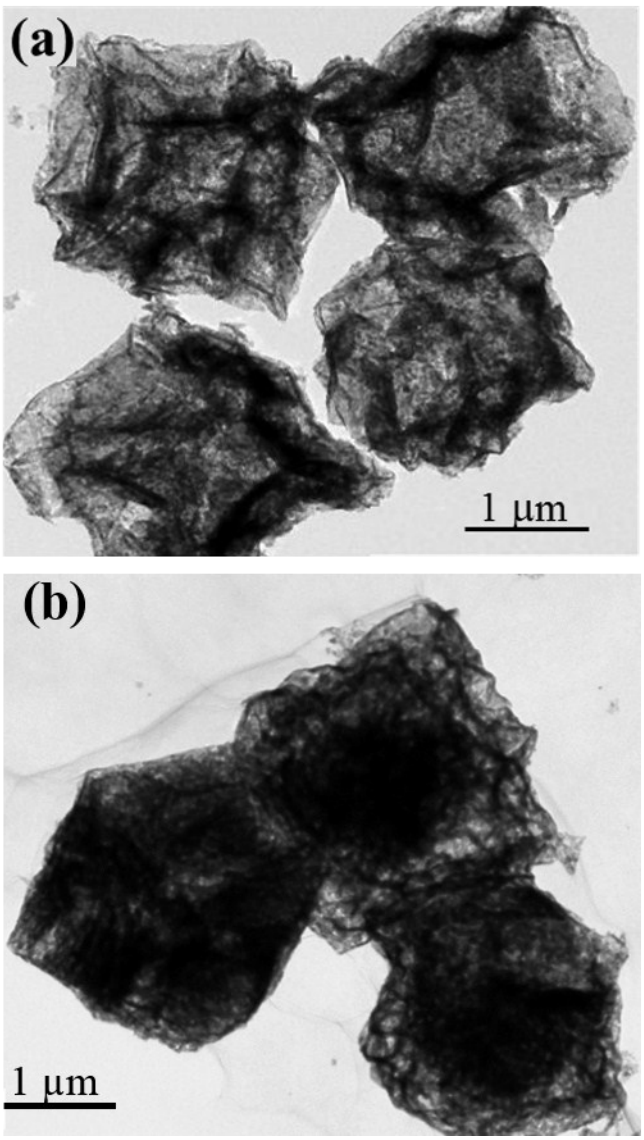


**Figure S7** TEM images of (a) N-$Co_3O_4$@N-C/GO and (b) N-$Co_3O_4$@N-C/rGO-S.

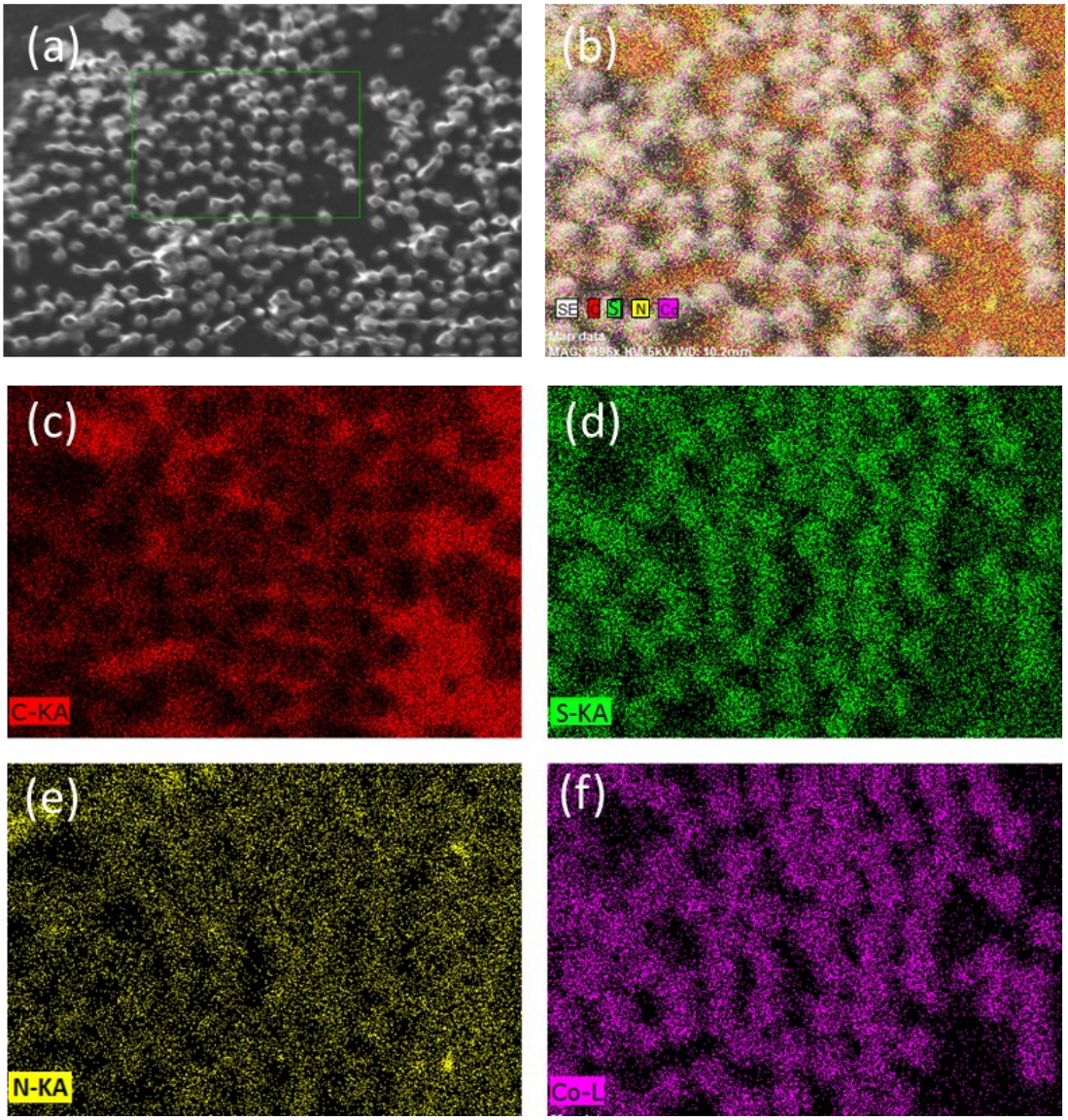


**Figure S8** (a) SEM image of N-$Co_3O_4$@N-C/rGO–S and the corresponding elemental mapping images of (b) Overall image (c) Carbon, (d) Sulfur, (e) Nitrogen, (f) Cobalt.

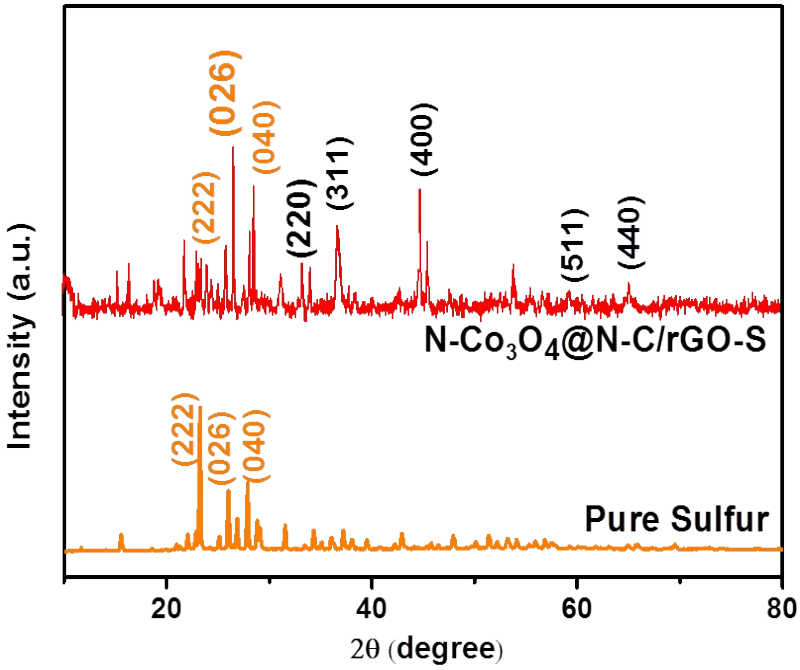


**Figure S9** XRD patterns of N-$Co_3O_4$@N-C/rGO-S, pure sulfur.

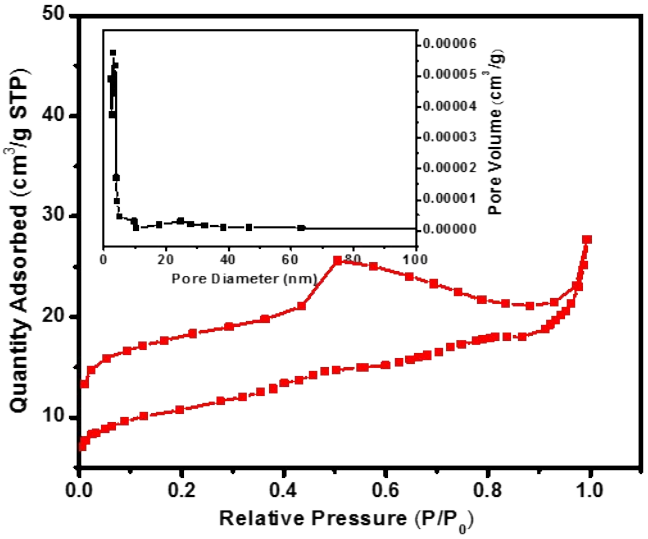


**Figure S10** Nitrogen adsorption-desorption isotherm curves of N-$Co_3O_4$@N-C/rGO-S.

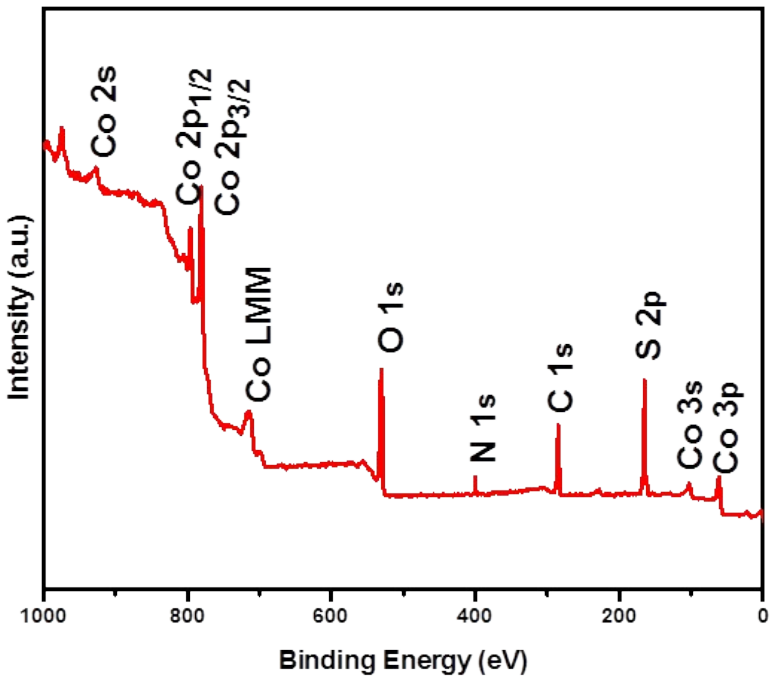


**Figure S11** XPS survey spectra of N-$Co_3O_4$@N-C/rGO-S, comfirming the existence of cobalt, oxygen, carbon, sulfur, nitrogen.

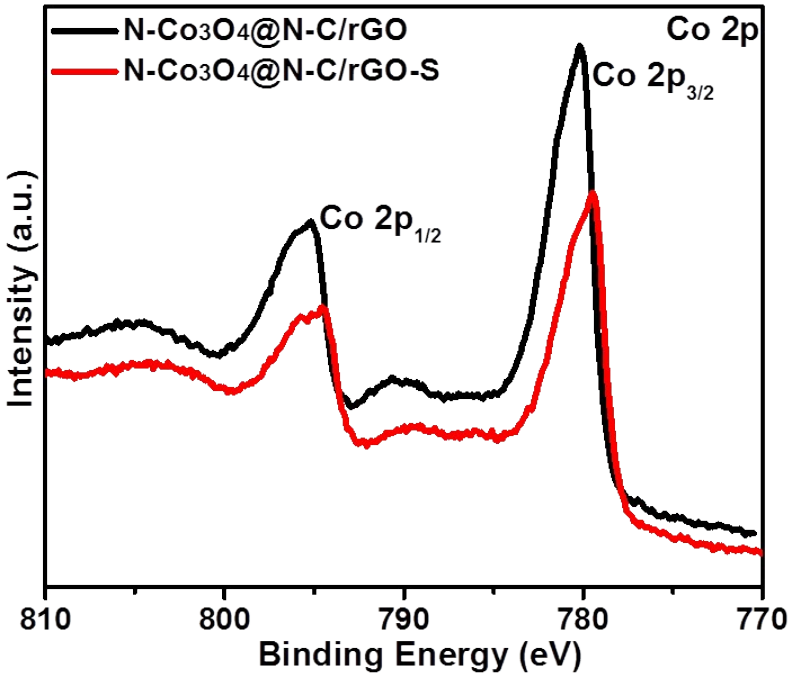


**Figure S12** XPS survey spectra of N-$Co_3O_4$@N-C/rGO-S, comfirming the existence of cobalt, oxygen, carbon, sulfur, nitrogen.

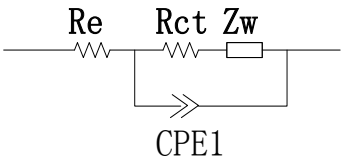


**Figure S13** The equivalent circuit of electrochemical impedance spectra in Figure 3b.

**Table S1** Parameters identification by modeling the impedance spectra in **Figure 3b**.

| Electrode | $R_e$ (ohm) | $R_{ct}$ (ohm) | Y1( $\Omega^{-1}cm^{-2}s^{-n}$) | n1 |
|---|---|---|---|---|
| N-$Co_3O_4$@N-C/rGO-S | 4.425 | 38.763 | 0.000035 | 0.79 |
| N-$Co_3O_4$@N-C-S | 4.578 | 41.687 | 0.000053 | |
| rGO-S | 4.08 | 52.732 | 0.000085 | |

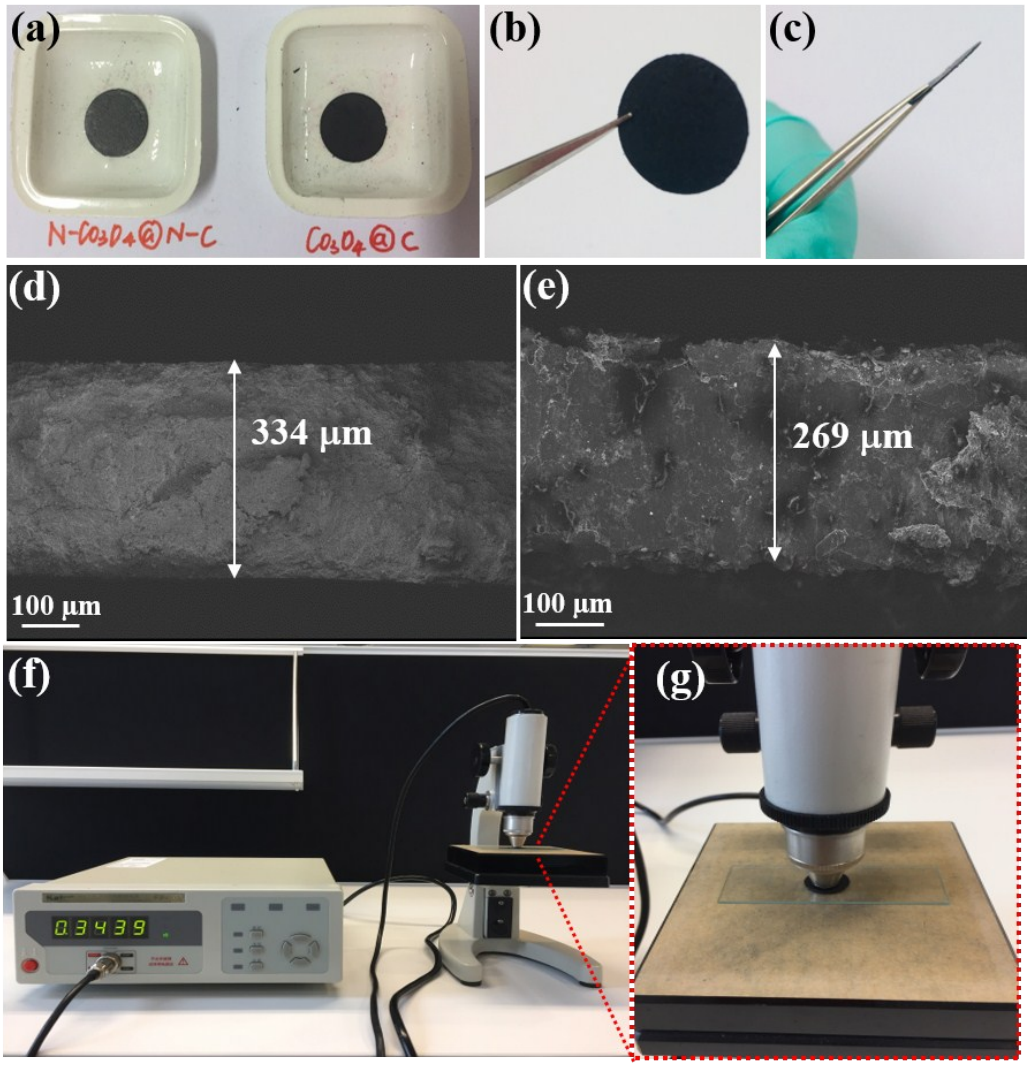


**Figure S14** (a) The pressed N-$Co_3O_4$@N-C and $Co_3O_4$@C disks. (b) Top view of the as-prepared disk. (c) Side view of the as-prepared disk. The cross-sectional view of (d) N-$Co_3O_4$@N-C disk and (e) $Co_3O_4$@C disks. (f ,g) Zhuhai Kaivo FP-001 Four-Point Probe Resistance Tester.

First, we pressed the N-$Co_3O_4$@N-C and $Co_3O_4$@C powder into disks, respectively. It should note that the $Co_3O_4$@C powder is made of commercial cobalt oxide mixed with the carbon black at the weight ratio of 9:1. We calculated the electronic conductivity of each sample based on the following equation:

The electronic conductivity for the N-$Co_3O_4$@N-C disks:

$\rho = R_\Omega \times W = R_x \times F(D/S) \times F(W/S) \times F_{sp} \times W$

$=0.1976 \times 10^3\ \Omega \times F(14/1) \times F(0.334/1) \times 1.004 \times 3.34 \times 10^{-6}$ m

$=0.1976 \times 10^3\ \Omega \times 4.348 \times 1 \times 1.004 \times 3.34 \times 10^{-6}$ m

$=2.881 \times 10^{-3} \Omega$ m

$\sigma = 1/\rho = 1/(2.881 \times 10^{-3})\ \Omega^{-1}\ m^{-1} = 347.1\ S\ m^{-1}$

The electronic conductivity for the $Co_3O_4$@ C disks:

$\rho = R_\Omega \times W = R_x \times F(D/S) \times F(W/S) \times F_{sp} \times W$

$=0.3454 \times 10^3\ \Omega \times F(14/1) \times F(0.269/1) \times 1.004 \times 2.69 \times 10^{-6}$ m

$=0.3454 \times 10^3\ \Omega \times 4.348 \times 1 \times 1.004 \times 2.69 \times 10^{-6}$ m

$=4.056 \times 10^{-3} \Omega$ m

$\sigma = 1/\rho = 1/(4.056 \times 10^{-3})\ \Omega^{-1}\ m^{-1} = 246.5\ S\ m^{-1}$

In the formular:

D: The diameter of the sample, in mm.

S: The distance between two neighbouring probes. The value S=1 mm for the four-point probe we use.

W: The thickness of the conductive layer, in mm.

$F_{sp}$: The probe distance correction factor. The value $F_{sp}$= 1.004 for the four-point probe we use.

F(D/S): The diameter correction factor. This factor can be chosen from the work brochure (**Table S2**) according to the value of D/S.

F(W/S): The thickness correction factor. This factor can be chosen from the work brochure (**Table S3**) according to the value of W/S.

$R_x$: The testing result from the tester.

$\rho$: The electrical resistivity.

$\sigma$: The electronic conductivity.

Therefore, the electronic conductivity of N-$Co_3O_4$@N-C and $Co_3O_4$@C powder are 347.1 and 246.5 S $m^{-1}$, respectively. It also further confirms that nitrogen doping promotes electron conductivity of the material.

**Table S2** The relationship between F(D/S) and D/S.

| The testing position / F（D/S） / D/S Value | centre point | In the middle of radius | 6mm from the edge |
|---|---|---|---|
| >200 | 4.532 | | |
| 200 | 4.531 | 4.531 | 4.462 |
| 150 | 4.531 | 4.529 | 4.461 |
| 125 | 4.530 | 4.528 | 4.460 |
| 100 | 4.528 | 4.525 | 4.458 |
| 76 | 4.526 | 4.520 | 4.455 |
| 60 | 4.521 | 4.513 | 4.451 |
| 51 | 4.517 | 4.505 | 4.447 |
| 38 | 4.505 | 4.485 | 4.439 |
| 26 | 4.470 | 4.424 | 4.418 |
| 25 | 4.470 | | |
| 22.22 | 4.454 | | |
| 20.00 | 4.436 | | |
| 18.18 | 4.417 | | |
| 16.67 | 4.395 | | |
| 15.38 | 4.372 | | |
| 14.28 | 4.348 | | |
| 13.33 | 4.322 | | |
| 12.50 | 4.294 | | |
| 11.76 | 4.265 | | |
| 11.11 | 4.235 | | |
| 10.52 | 4.204 | | |
| 10.00 | 4.171 | | |

**Table S3** The relationship between F(W/S) and W/S.

| W/S | F (W/S) | W/S | F (W/S) | W/S | F (W/S) | W/S | F (W/S) |
|---|---|---|---|---|---|---|---|
| <0.400 | 1.0000 | 0.530 | 0.9962 | 0.665 | 0.9858 | 0.800 | 0.9663 |
| 0.400 | 0.9997 | 0.535 | 0.9960 | 0.670 | 0.9853 | 0.805 | 0.9654 |
| 0.405 | 0.9996 | 0.540 | 0.9957 | 0.675 | 0.9847 | 0.810 | 0.9644 |
| 0.410 | 0.9996 | 0.545 | 0.9955 | 0.680 | 0.9841 | 0.815 | 0.9635 |
| 0.415 | 0.9995 | 0.550 | 0,9952 | 0.685 | 0.9835 | 0.820 | 0.9626 |
| 0.420 | 0.9994 | 0.555 | 0.9949 | 0.690 | 0.9829 | 0.825 | 0.9616 |
| 0.425 | 0.9993 | 0.560 | 0.9946 | 0.695 | 0.9823 | 0.830 | 0.9607 |
| 0.430 | 0.9993 | 0.565 | 0.9943 | 0.700 | 0.9817 | 0.835 | 0.9597 |
| 0.435 | 0.9992 | 0.570 | 0.9940 | 0.705 | 0.9810 | 0.840 | 0.9587 |
| 0.440 | 0.9991 | 0.575 | 0.9937 | 0.710 | 0.9804 | 0.845 | 0.9577 |
| 0.445 | 0.9990 | 0.580 | 0.9934 | 0.715 | 0.9797 | 0.850 | 0.9567 |
| 0.450 | 0.9989 | 0.585 | 0.9930 | 0.720 | 0.9790 | 0.855 | 0.9557 |
| 0.455 | 0.9988 | 0.590 | 0.9927 | 0.725 | 0.9783 | 0.860 | 0.9546 |
| 0.460 | 0.9987 | 0.595 | 0.9923 | 0.730 | 0.9776 | 0.865 | 0.9536 |
| 0.465 | 0.9985 | 0.600 | 0.9919 | 0.735 | 0.9769 | 0.870 | 0.9525 |
| 0.470 | 0.9984 | 0.605 | 0.9915 | 0.740 | 0.9761 | 0.875 | 0.9514 |
| 0.475 | 0.9983 | 0.610 | 0.9911 | 0.745 | 0.9754 | 0.880 | 0.9504 |
| 0.480 | 0.9981 | 0.615 | 0.9907 | 0.750 | 0.9746 | 0.885 | 0.9493 |
| 0.485 | 0.9980 | 0.620 | 0.9903 | 0.755 | 0.9738 | 0.890 | 0.9482 |
| 0.490 | 0.9978 | 0.625 | 0.9898 | 0.760 | 0.9731 | 0.895 | 0.9471 |
| 0.495 | 0.9976 | 0.630 | 0.9894 | 0.765 | 0.9723 | 0.900 | 0.9459 |
| 0.500 | 0.9975 | 0.635 | 0.9889 | 0.770 | 0.9714 | 0.905 | 0.9448 |
| 0.505 | 0.9973 | 0.640 | 0.9884 | 0.775 | 0.9706 | 0.910 | 0.9437 |
| 0.510 | 0.9971 | 0.645 | 0.9879 | 0.780 | 0.9698 | 0.915 | 0.9425 |
| 0.515 | 0.9969 | 0.650 | 0.9874 | 0.785 | 0.9689 | 0.920 | 0.9413 |
| 0.520 | 0.9967 | 0.655 | 0.9869 | 0.790 | 0.9680 | 0.925 | 0.9402 |
| 0.525 | 0.9965 | 0.660 | 0.9864 | 0.795 | 0.9672 | 0.930 | 0.9390 |
| 0.935 | 0.9378 | 1.10 | 0.8939 | 1.85 | 0.6718 | 2.60 | 0.5098 |
| 0.940 | 0.9366 | 1.15 | 0.8793 | 1.90 | 0.6588 | 2.65 | 0.5013 |
| 0.945 | 0.9354 | 1.20 | 0.8643 | 1.95 | 0.6460 | 2.70 | 0.4931 |
| 0.950 | 0.9342 | 1.25 | 0.8491 | 2.00 | 0.6337 | 2.75 | 0.4851 |
| 0.955 | 0.9329 | 1.30 | 0.8336 | 2.05 | 0.6216 | 2.80 | 0.4773 |
| 0.960 | 0.9317 | 1.35 | 0.8181 | 2.10 | 0.6099 | 2.85 | 0.4698 |
| 0.965 | 0.9304 | 1.40 | 0.8026 | 2.15 | 0.5986 | 2.90 | 0.4624 |
| 0.970 | 0.9292 | 1.45 | 0.7872 | 2.20 | 0.5875 | 2.95 | 0.4553 |
| 0.975 | 0.9279 | 1.50 | 0.7719 | 2.25 | 0.5767 | 3.00 | 0.4484 |
| 0.980 | 0.9267 | 1.55 | 0.7568 | 2.30 | 0.5663 | 3.2 | 0.422 |
| 0.985 | 0.9254 | 1.60 | 0.7419 | 2.35 | 0.5562 | 3.4 | 0.399 |
| 0.990 | 0.9241 | 1.65 | 0.7273 | 2.40 | 0.5464 | 3.6 | 0.378 |
| 0.995 | 0.9228 | 1.70 | 0.7130 | 2.45 | 0.5368 | 3.8 | 0.359 |
| 1.00 | 0.9215 | 1.75 | 0.6989 | 2.50 | 0.5275 | 4.0 | 0.342 |

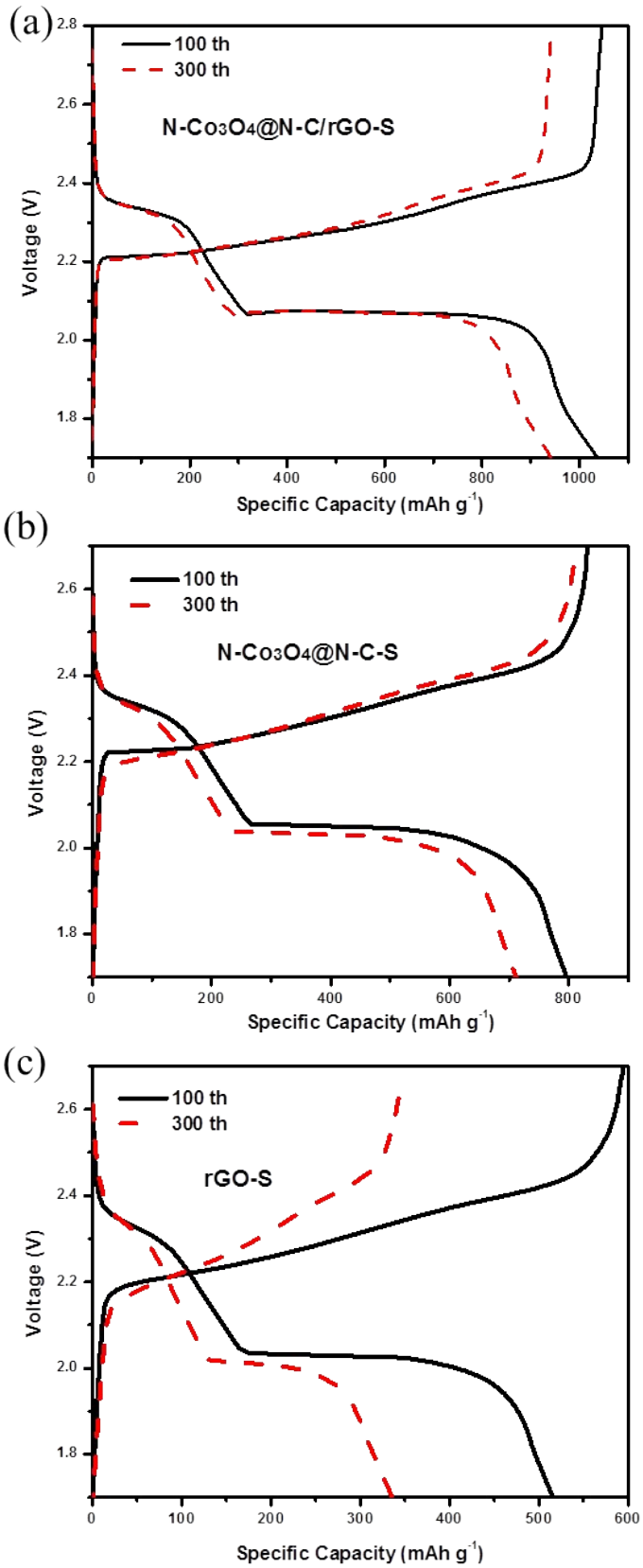


**Figure S15** The 100th and 300th cycle galvanostatic charge/discharge voltage profiles at 0.2 C. (a) N-$Co_3O_4$@N-C/rGO -S, (b) N-$Co_3O_4$@N-C-S, (c) rGO-S.

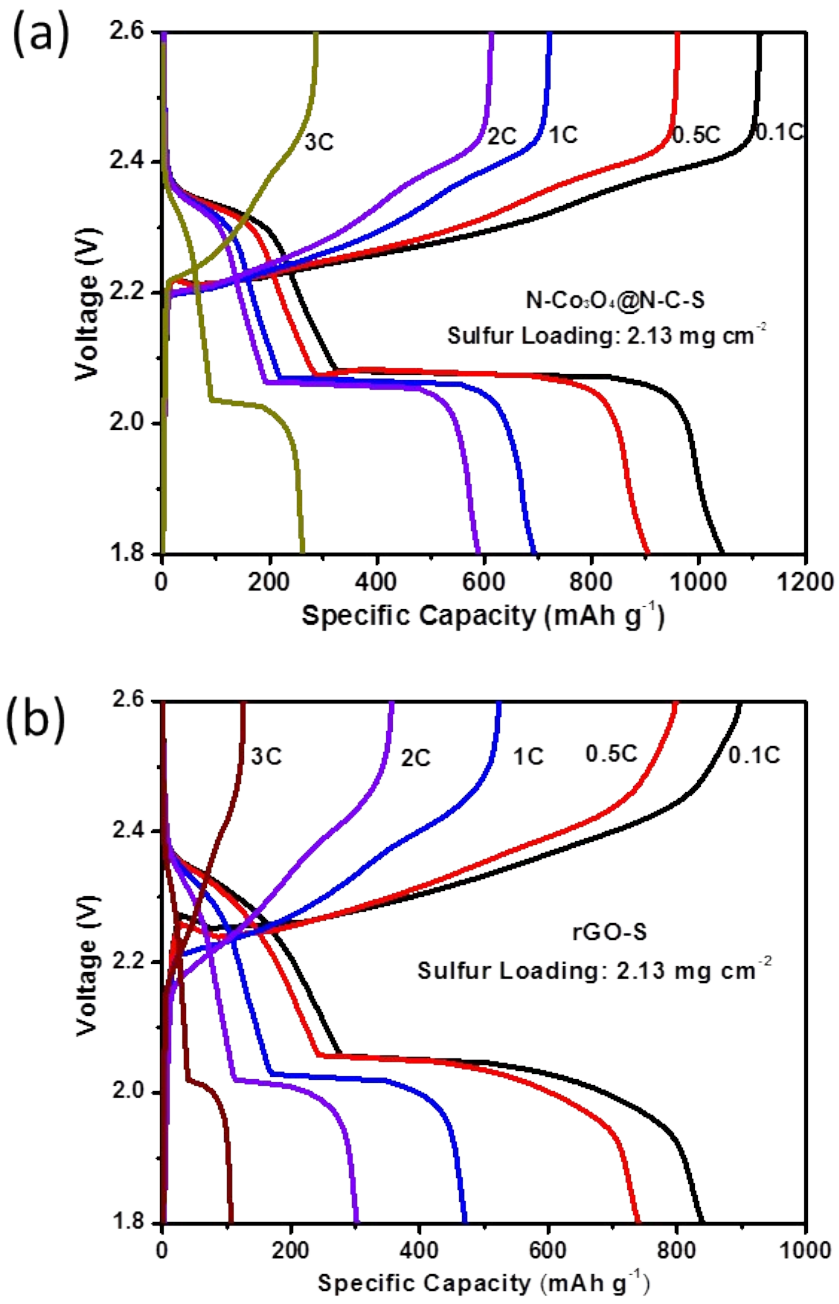


**Figure S16** The galvanostatic charge/discharge voltage profiles of N-$Co_3O_4$@N-C-S, rGO-S cathodes at various current densities from 0.1 C to 3 C.

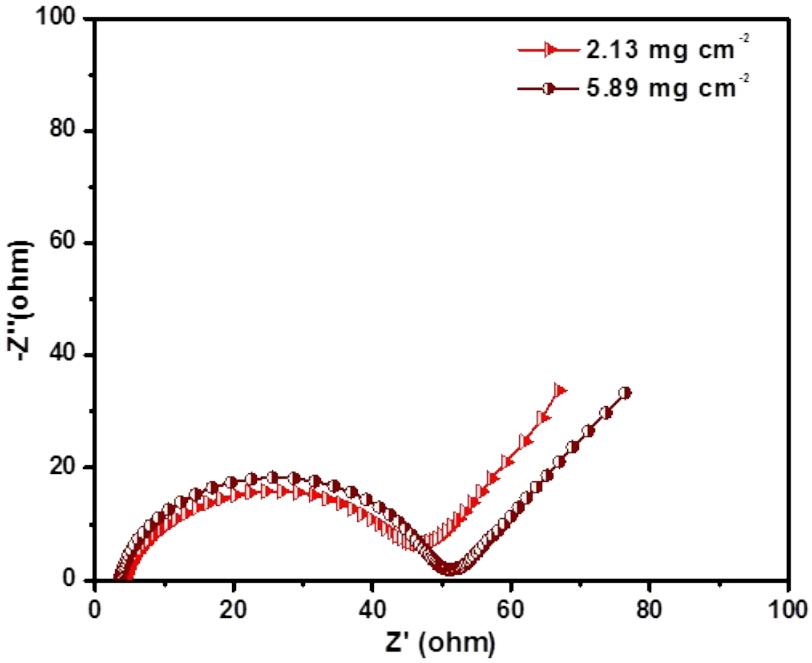


**Figure S17** Nyquist plots of N-$Co_3O_4$@N-C/rGO-S with the sulfur loading of 2.13 mg $cm^{-2}$, 5.89 mg $cm^{-2}$ cathode electrodes.

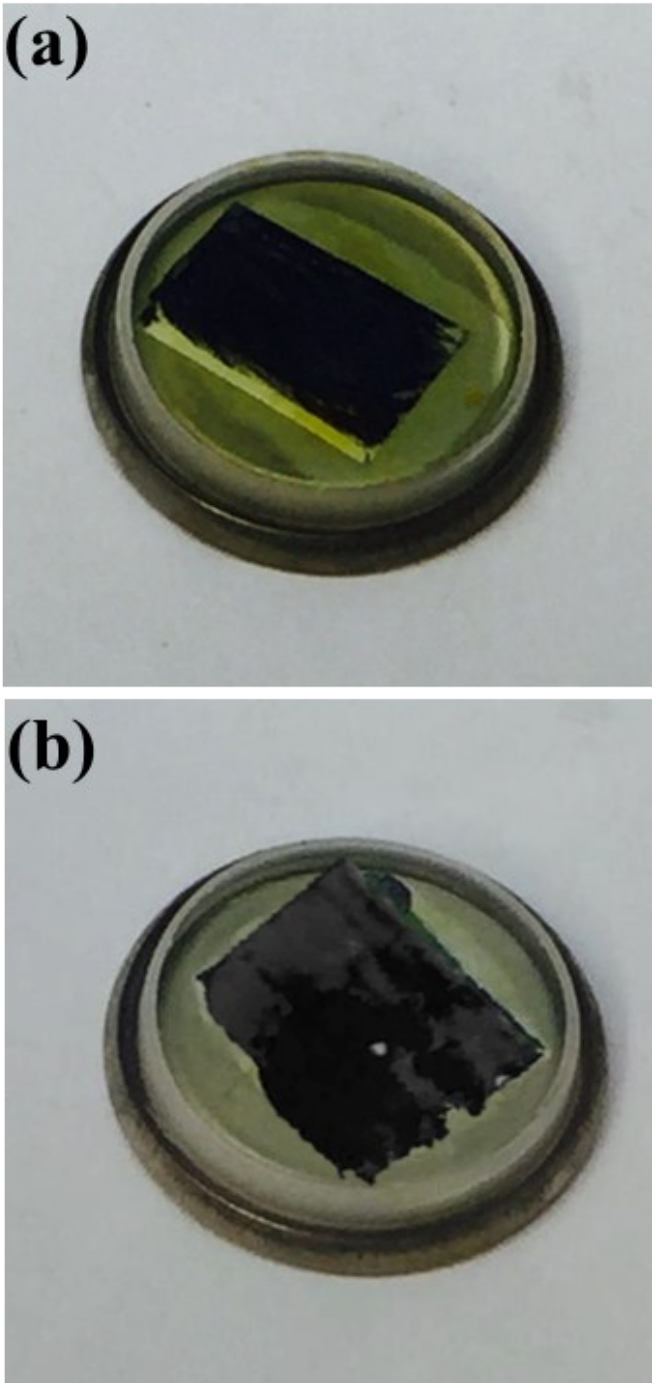


**Figure S18** (a) Dissembled electrode of rGO-S after 50 cycles. (b) Dissembled electrode of N-$Co_3O_4$@N-C/rGO-S after 50 cycles.