Electronic Supplementary Material (ESI) for Nanoscale.
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Supporting information

Cobalt sulfide/N, S Co-doped porous carbon core-shell nanocomposites as superior bifunctional electrocatalysts for oxygen reduction and evolution reactions

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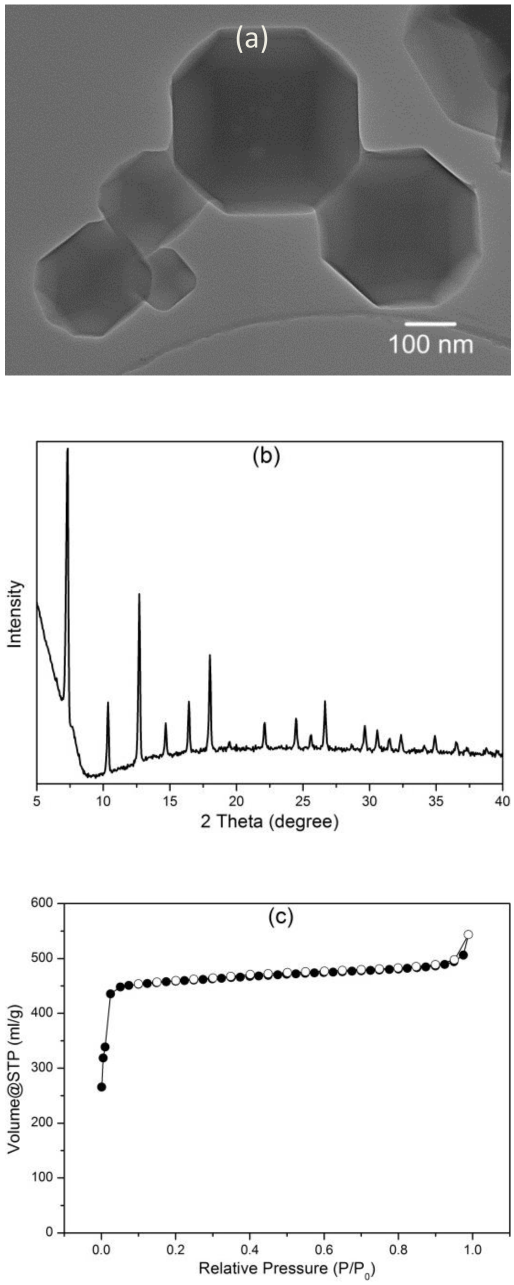

Figure. S1 (a) TEM image, (b) powder XRD pattern and (c) nitrogen sorption isotherms of the parental ZIF-67 material.

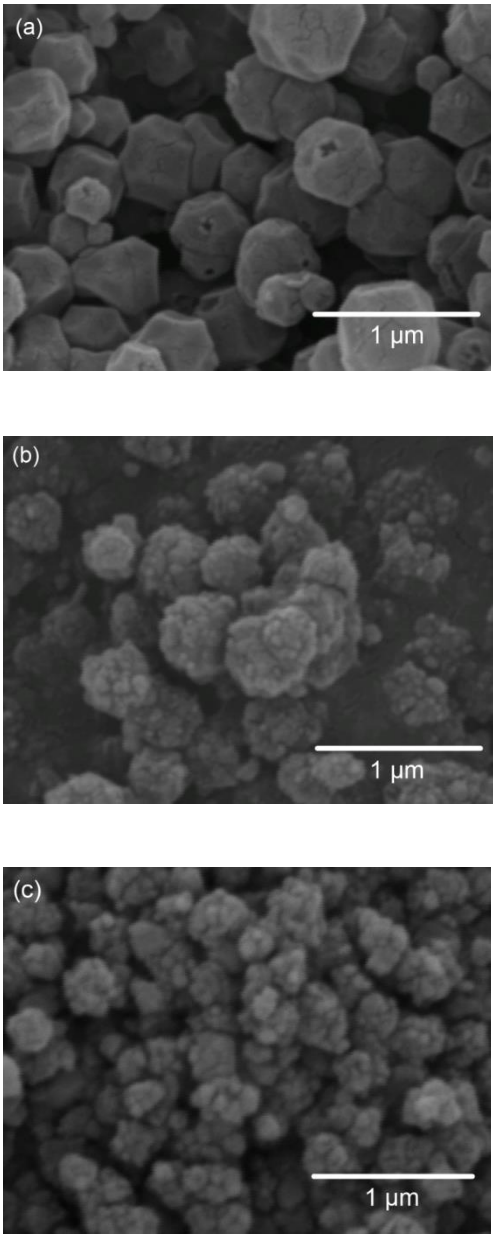

Figure. S2 SEM images of the as-synthesized nanocomposites where (a) Co_xS_y@C-600; (b) Co_xS_y@C-800 and (c) Co_xS_y@C-1000.

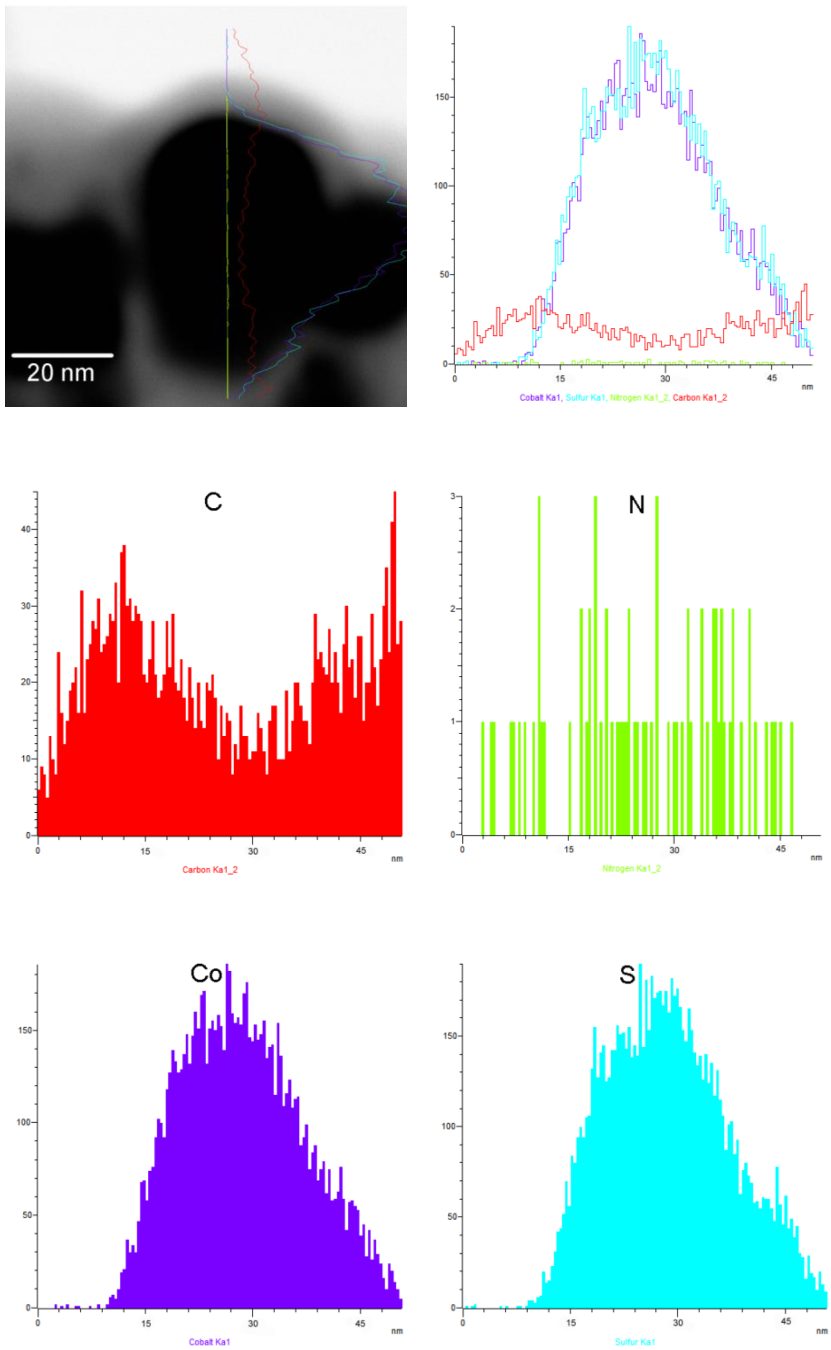

Figure. S3 STEM image and linear EDX for sample Co_xS_y@C-1000. C, N, S and Co signals are clearly detected from the sample. The compositional line profile shows that while C signal is observed on the outer surface of cobalt sulfide particles, S and Co signals are detected only in the inner core of the nanoparticles. The results indicate that the nanoparticle consists of a cobalt sulfide core, surrounded by a 5 nm thickness of carbon shell.

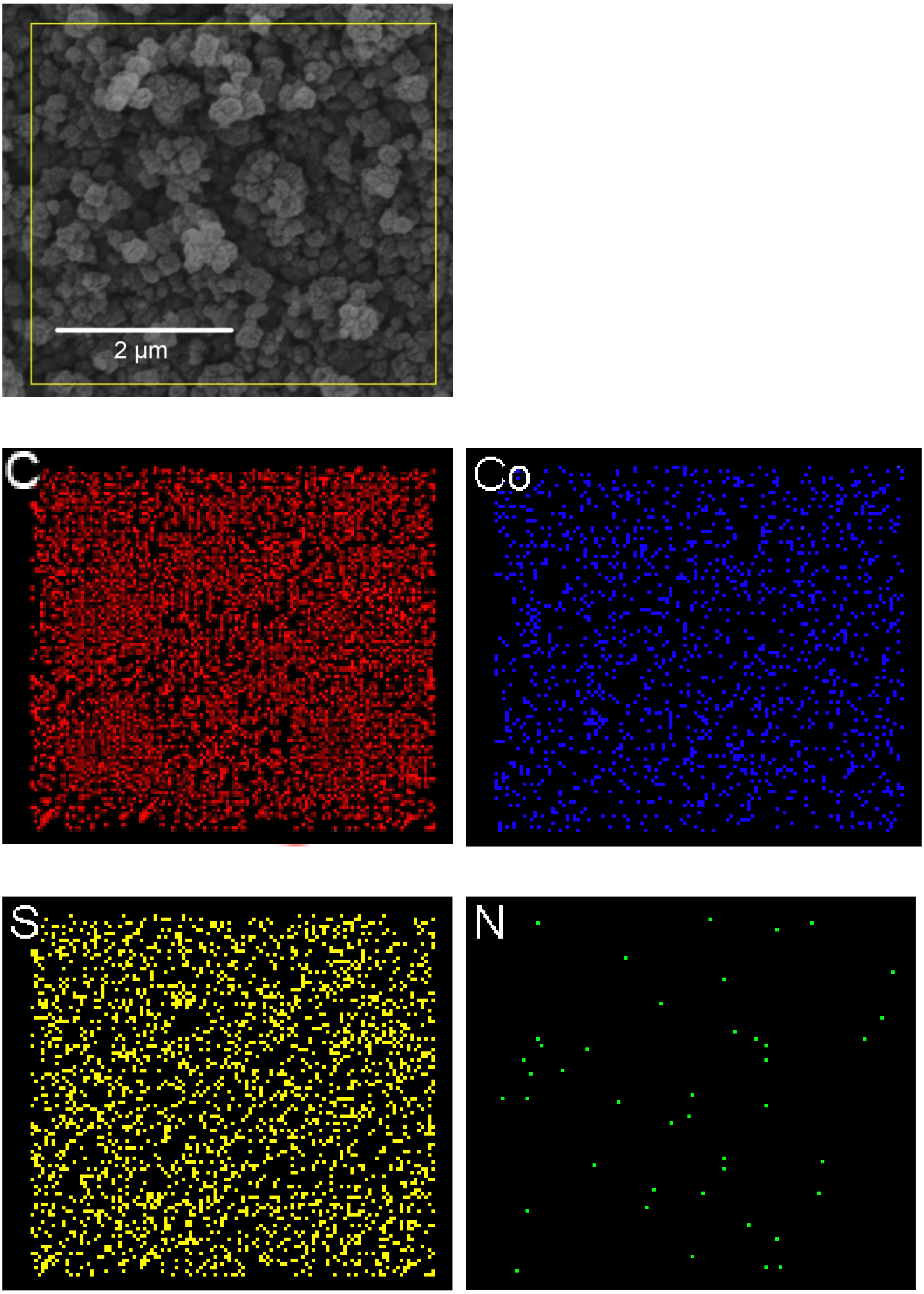

Figure. S4 SEM image and elemental mappings for sample Co_xS_y@C-1000.

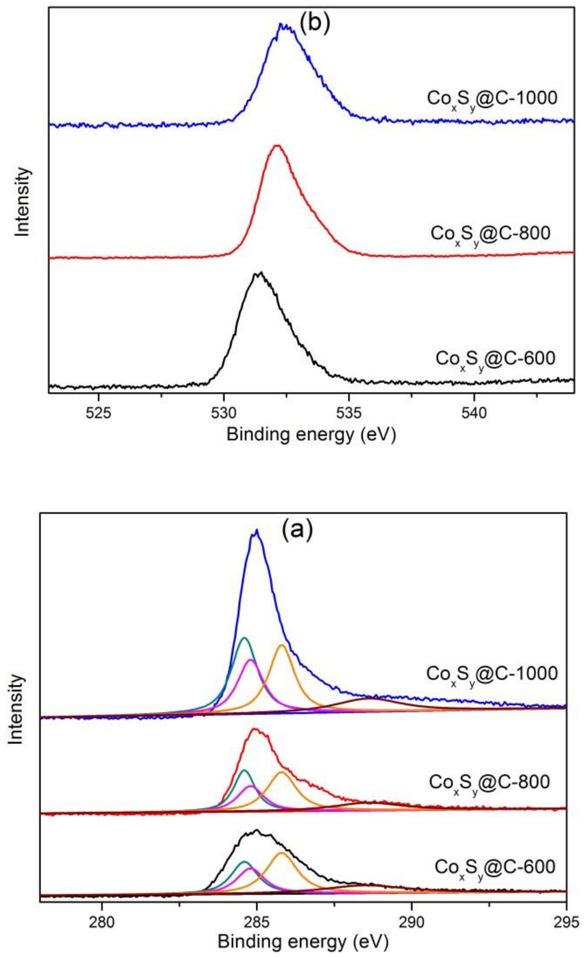

Figure. S5 XPS results of (a) C 1s, and (b) O 1s for the as-synthesized nanocomposites.

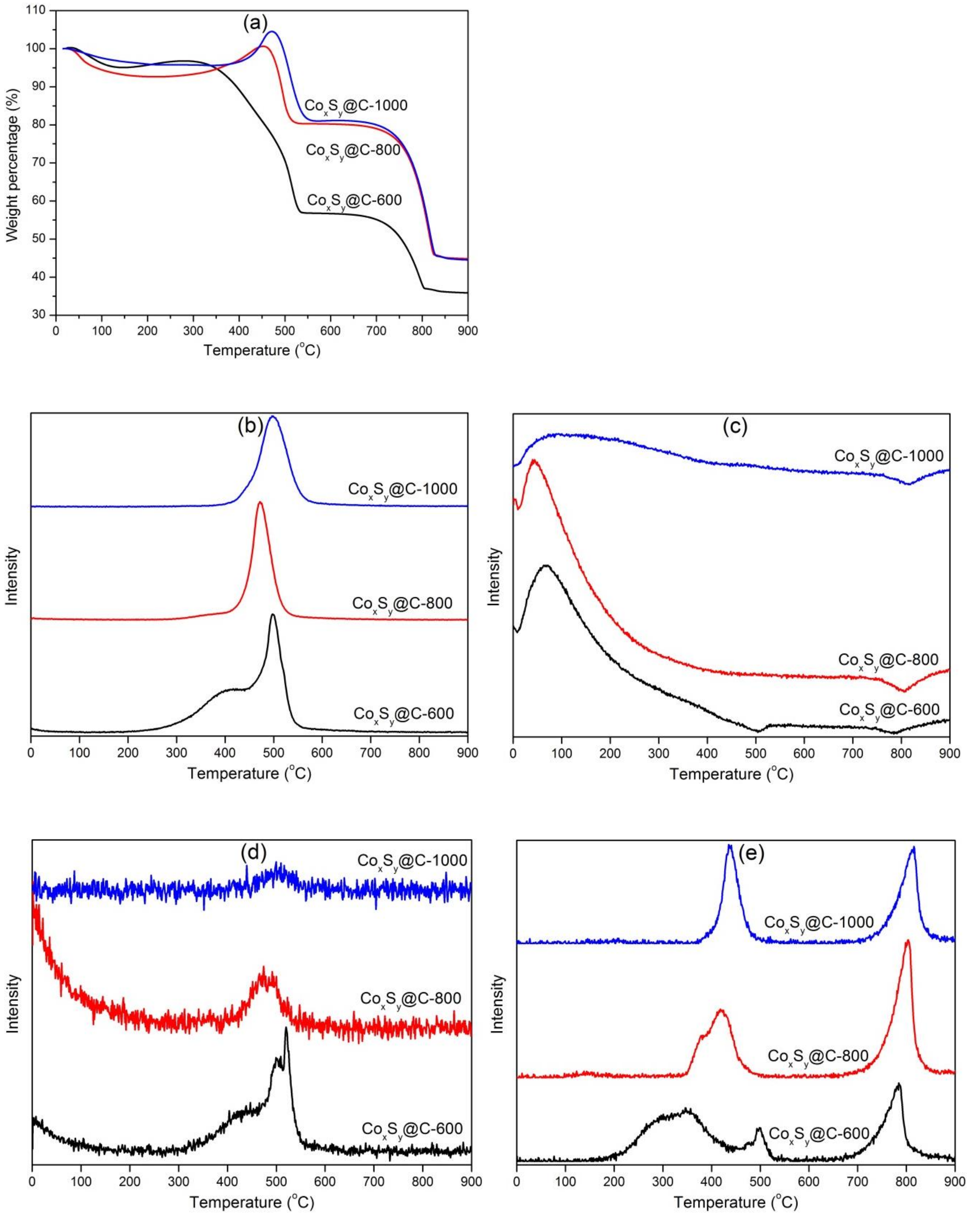

Figure. S6 TGA (a) and their corresponding MS curves of CO_2 (b), H_2O (c), NO_2 (d), and SO_2 (e) for different nanocomposites.

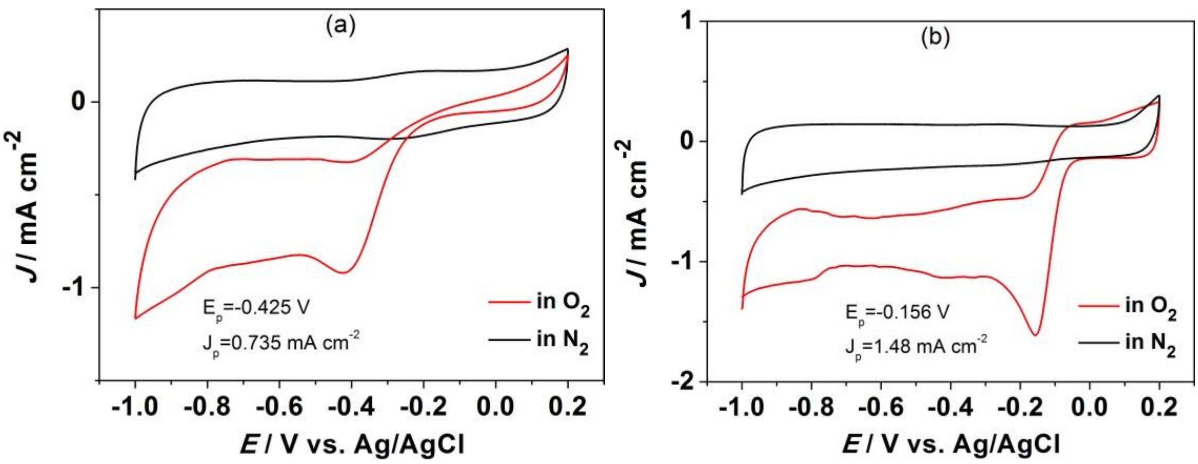

Figure. S7 CV curves of (a) Co_xS_y@C-600, and (b) Co_xS_y@C-800 nanocomposites in N_2-saturated and O_2-saturated 0.1M KOH solution.

The kinetics parameters can be analyzed with the K-L equations as following:[1,2]

$$\frac{1}{J} = \frac{1}{J_{\mathrm{K}}} + \frac{1}{B\omega^{1/2}}$$

$$B = 0.62nFC_0D_0^{2/3}\upsilon^{-1/6}$$

Where J is the measured current density, J_{K} is the kinetic current density, ω is the angular velocity of the rotating electrode, B is the Levich constant, n is the overall number of electron transferred in the ORR process, F is the Faraday constant (96485 C mol^{-1}), C_0 is the bulk concentration of O_2 (1.2×10^{-6} mol cm^{-3}), D_0 is the diffusion coefficient of O_2 (1.9×10^{-5} cm^2 s^{-1}) and υ is the kinematic viscosity (0.01 cm^2 s^{-1}) of the electrolyte.

The electron transfer number and the peroxide percentage can be calculated by the equations as following:[1,2]

$$\mathrm{H_2O_2}(\%) = 200 \times \frac{I_{\mathrm{r}}/N}{I_{\mathrm{d}} + I_{\mathrm{r}}/N}$$

$$n = 4 \times \frac{I_{\mathrm{d}}}{I_{\mathrm{d}} + I_{\mathrm{r}}/N}$$

Where I_d is disk current, I_r is ring current and N is the current collection efficiency (0.37) of the Pt ring.

References

(1) Li, Q.; Zhang, S.; Dai, L.; Li, L.-s. *J. Am. Chem. Soc.* **2012**, *134*, 18932.

(2) Paulus, U. A.; Schmidt, T. J.; Gasteiger, H. A.; Behm, R. J. *J. Electroanal. Chem.* **2001**, *495*, 134.

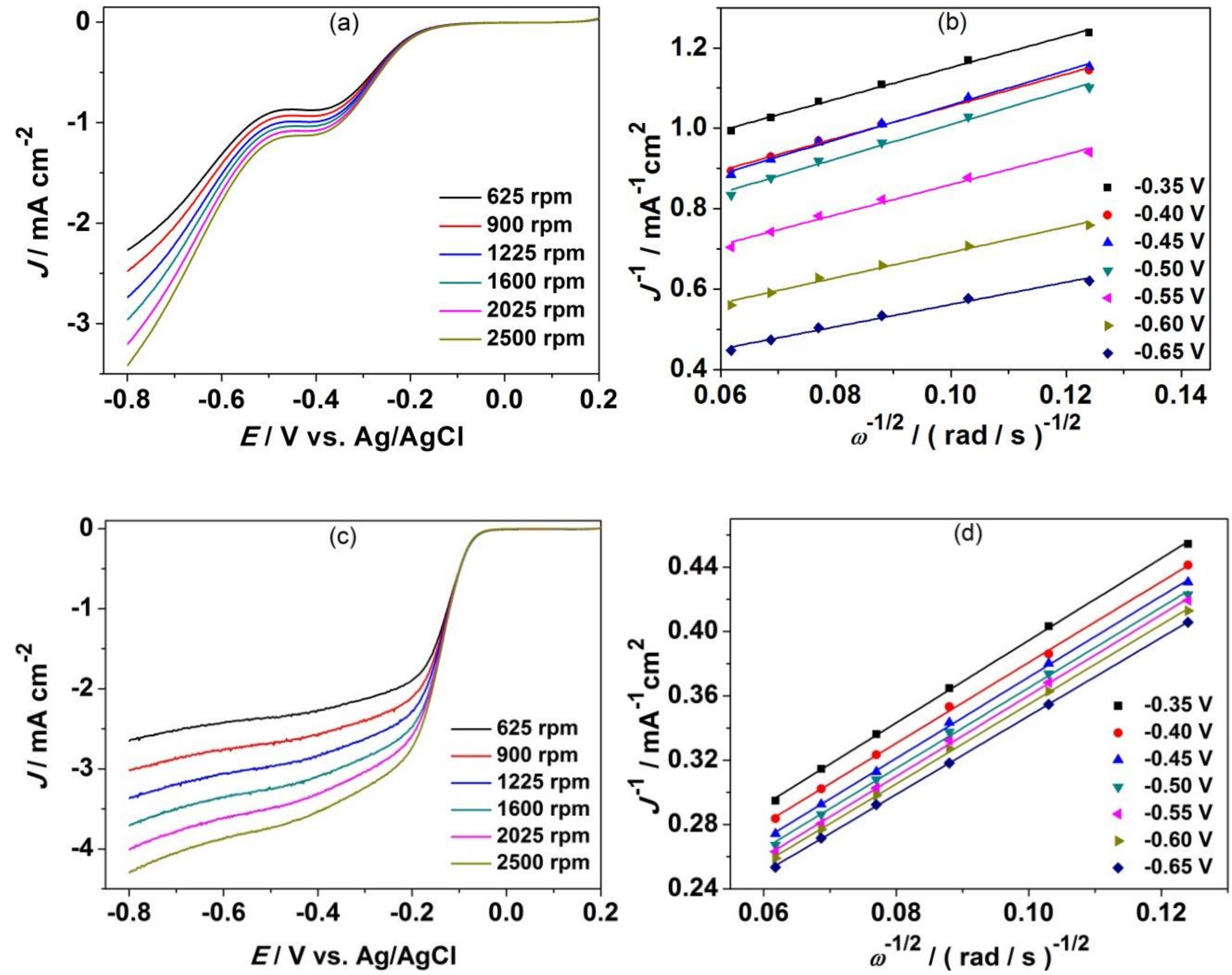

Figure. S8 ORR polarization curves (a) and (c) of Co_xS_y@C-600, Co_xS_y@C-800, at different rotating speeds, respectively. K-L plots (b) and (d) of Co_xS_y@C-600 and Co_xS_y@C-800 at different potentials.

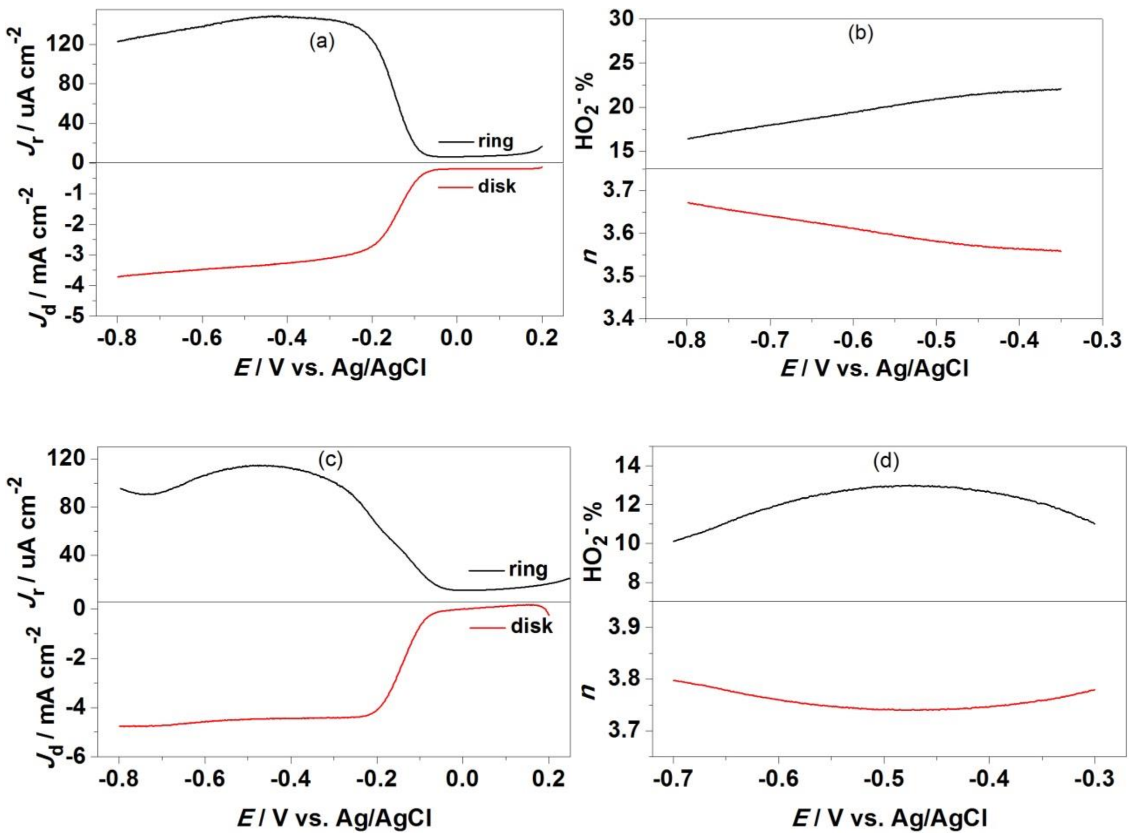

Figure. S9 (a) Disk current and ring current from RRDE measurements of Co_xS_y@C-800 with various loadings in O_2-saturated 0.1M KOH at a rotating speed of 1600rpm. (b) Percentage of 2e reduction and electron transfer number n in ORR at different potentials calculated from RRDE curves in (a). (c) Disk current and ring current from RRDE measurements of Co_xS_y@C-1000 with various loadings in O_2-saturated 0.1M KOH at a rotating speed of 1600rpm. (d) Percentage of 2e reduction and electron transfer number n in ORR at different potentials calculated from RRDE curves in (c).

Table S1 Textural properties of the as-synthesized Co_xS_y@C composites.

	Specific surface area (m^2 g^{-1})	Microporous surface area (m^2 g^{-1})	External surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Micropore volume (cm^3 g^{-1})
Co_xS_y@C-600	178	19	159	0.80	0.008
Co_xS_y@C-800	238	92	146	0.35	0.038
Co_xS_y@C-1000	248	39	209	0.31	0.019

Table S2 Comparison of the ORR catalytic performance between our materials and different previous catalysts in 0.1 M KOH (Electrode rotating speed is 1600 rpm).

References	Catalyst	Onset potential (V vs. RHE)*	Current density (mA cm^{-2} at 0.45 V vs. RHE)	Number of electron transfer
This work	Co_xS_y@C-1000	0.92	-4.50	3.69-3.78
Angew. Chem. Int. Ed. 2011, 50, 10969	$Co_{1-x}S$/RGO	0.87	-5.4	4-4.1
Chem. Eur. J. 2013, 19, 5183	Co_3S_4/graphene	0.91	-3.2	3.2-3.9
ACS Appl. Mater. Interfaces, 2015, 7, 1207	$Co_{0.5}Fe_{0.5}S$@N-MC	0.91	-5.6	3.8-4.0
ACS Appl. Mater. Interfaces 2013, 5, 5002	$NiCo_2S_4$@N/S-rGO	0.85	-4.1	3.6-3.8
J. Mater. Chem. A 2013, 1, 5741	CoS_2	0.80	-3.4	average 3.8
Adv. Funct. Mater. 2015, 25, 872	N/Co-doped PCP//NRGO	0.97	-7.9	3.90-3.94

* Potentials measured versus Ag/AgCl electrode were converted to a reversible hydrogen electrode (RHE) scale on the basis of Nernst equation as follows:

$$E_{RHE} = E_{Ag/AgCl} + 0.059(pH) + 0.197(V)$$

Table S3 Comparison of the OER catalytic performances between our materials and different previous catalysts.

References	Catalyst	Potential (V vs. RHE) acquired for the current density of 10 mA cm^{-2}	Electrolyte
This work	Co_xS_y@C-800	1.86	0.1 M KOH
This work	Co_xS_y@C-1000	1.70	0.1 M KOH
ACS Appl. Mater. Interfaces, 2015, 7, 1207	$Co_{0.5}Fe_{0.5}S$@N-MC	1.64	1 M KOH
ACS Appl. Mater. Interfaces 2013, 5, 5002	$NiCo_2S_4$@N/S-rGO	1.69	0.1 M KOH
Adv. Funct. Mater. 2015, 25, 872	N/Co-doped PCP//NRGO	1.66	0.1 M KOH
Small, 2014, 10, 2251	NGSH	1.63	0.1 M KOH
J. Am. Chem. Soc., 2010, *132*, 13612	$CaMn_4O_x$	1.77	0.1 M KOH
J. Phys. Chem. Lett., 2012, *3*, 399	r-IrO_2	~1.73 or 1.68	0.1 M KOH or 0.1 M $HClO_4$