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Enhancing performance in sandwich-like cobalt sulfide and carbon for quasi-solid-state hybrid electrochemical capacitors†

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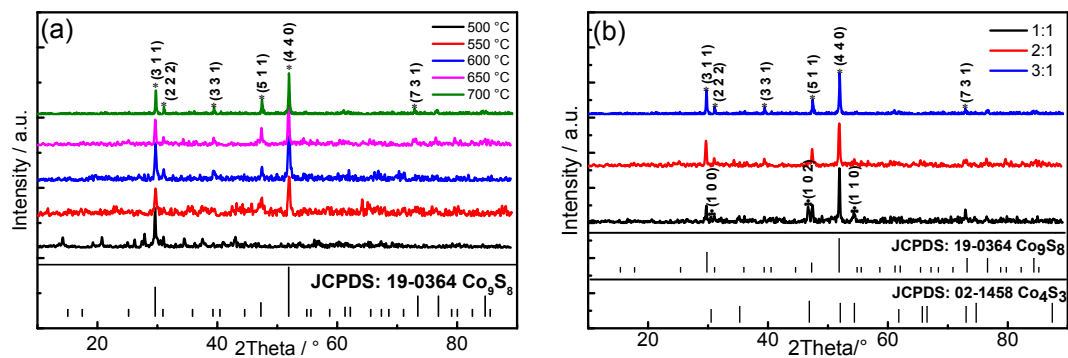


Figure S1 XRD patterns of the samples annealed under (a) different temperatures and (b) different formulas.

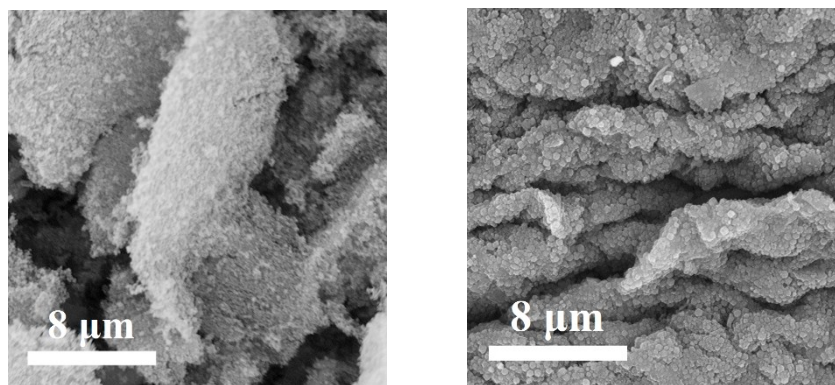
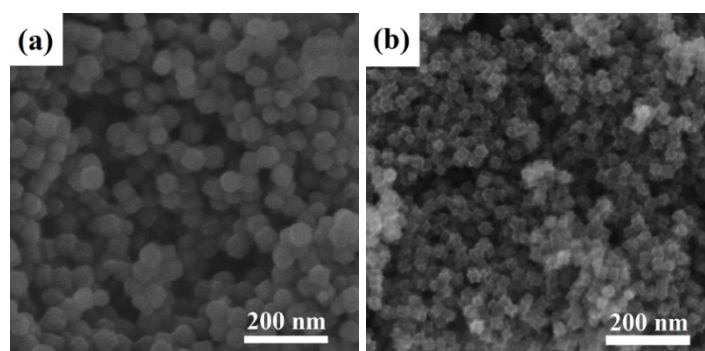


Figure S2 SEM images of (a) ZIF-8/GO and (b) ZIF-67/GO.



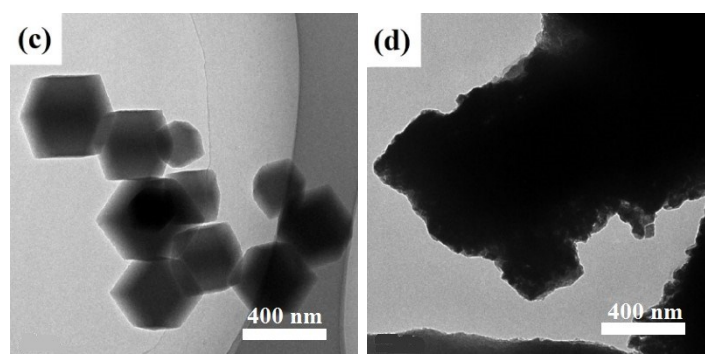


Figure S3 SEM images of (a) ZIF-8 nanocrystals and (b) PC derived from ZIF-8. The ZIF-8 nanocrystals are polyhedral in shapes with sizes of around 50 nm. After carbonization, the PC individuals having shrunk surfaces show an average size of 30 nm. TEM images of (c) ZIF-67 nanocrystals and (d) $\text{Co}_x\text{S}@PC$ derived from ZIF-67. The ZIF-67 nanocrystals present polyhedral shapes with an average size of 400 nm. As shown, after sulfidation, the $\text{Co}_x\text{S}@PC$ nanocrystals agglomerate seriously. The scale bars are 200 nm and 400 nm in (a) (b) and (c) (d), respectively.

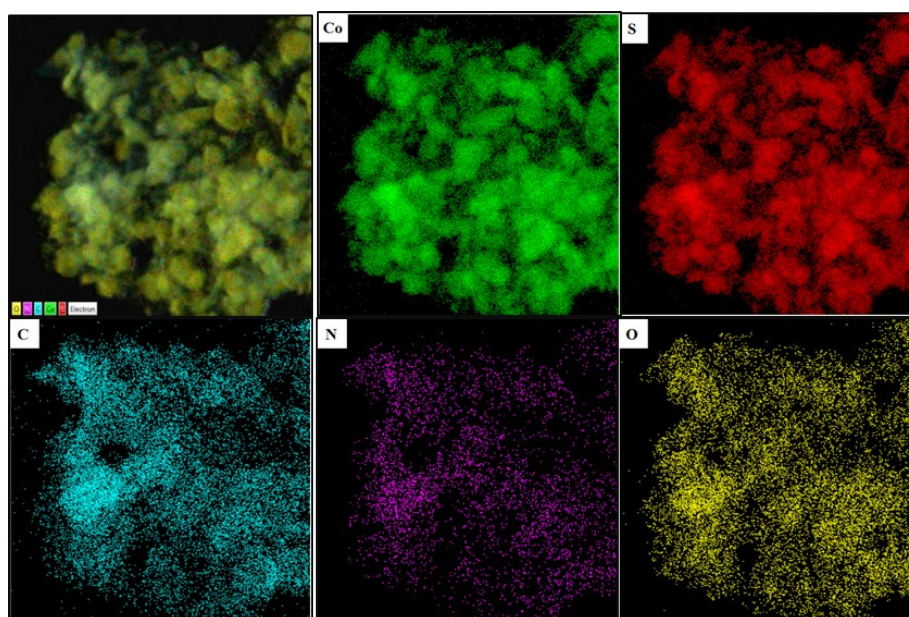


Figure S4 EDX mappings of $\text{Co}_x\text{S}@PC/RGO$. All of the selected elements distribute uniformly. Co and S are embedded in the N-doped C matrix.

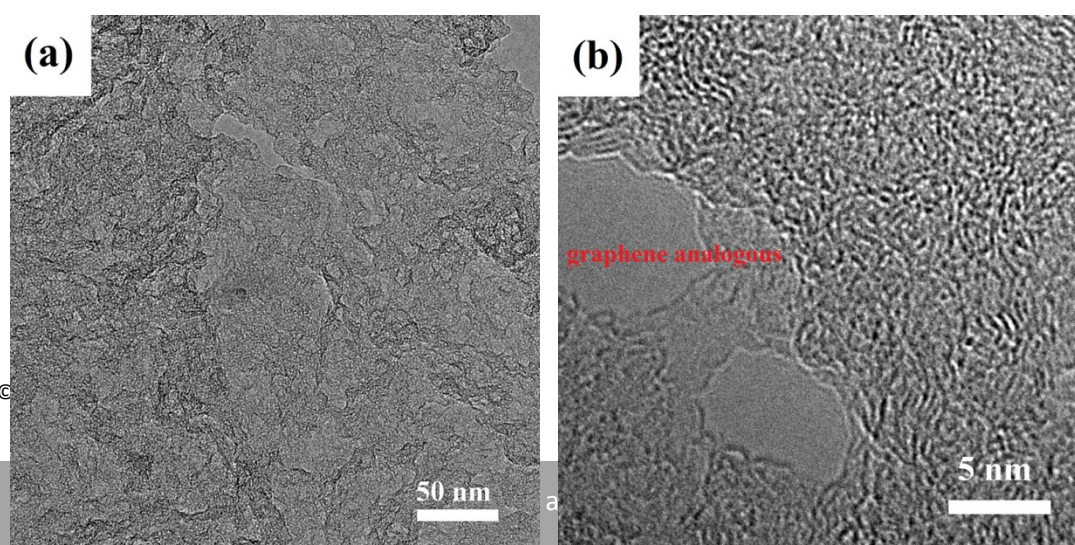


Figure S5 (a) TEM image and (b) high-resolution TEM image of PC/RGO. Mesopores distribute uniformly on the surface of porous carbon. Graphene analogous particles derived from the ZIF-8 can be observed. The scale bars in (a) and (b) are 50 and 5 nm, respectively.

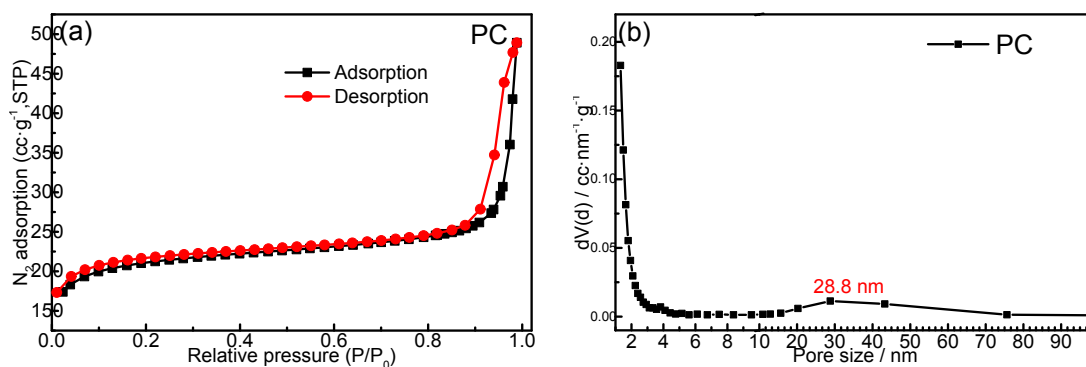


Figure S6 (a) Nitrogen sorption isotherms and (b) PSD curves of PC. The sorption-desorption isotherms exhibit a sharp rise in the low pressure area (typical for microporous material). The PSD curves evaluated by BJH model are in accordance with the intrinsic porous structures of ZIF-8 nanocrystals.

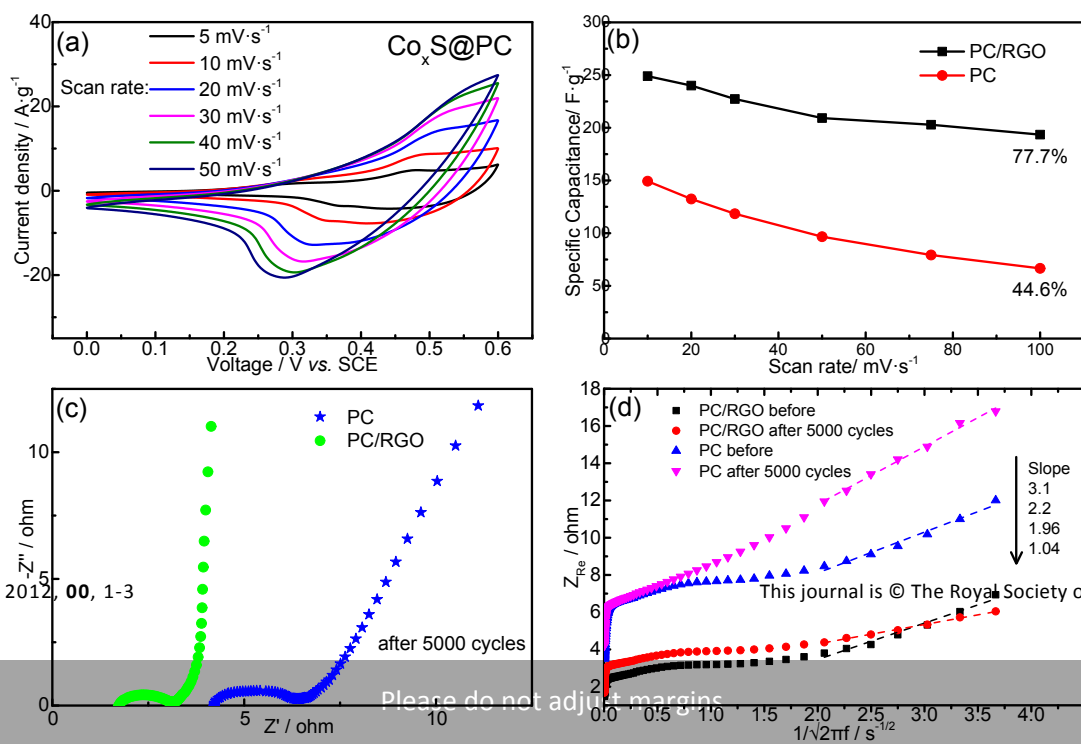


Figure S7 (a) CV curves of $\text{Co}_x\text{S}@PC$. (b) Capacitances of PC/RGO and PC at various potential scan rates. (c) Nyquist impedance plots for PC/RGO and PC after 5000 cycles. (d) Relationships between Z_{Re} and frequency for these electrodes and the fitted lines about Warburg coefficients. Z_{Re} is the real part of total resistance (see more in Note S2). The EIS spectra were tested in a frequency region of 0.01 - 100000 Hz.

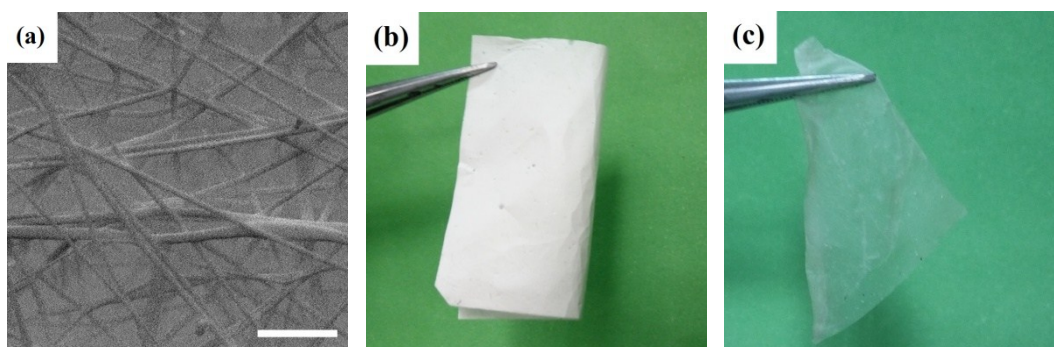


Figure S8 (a) SEM image of the PVA-PAA membrane. The scale bar is 4 μm . Photos of the membrane (b) before and (c) after electrolyte soaking. It turns to be transparent after soaking, indicating its superior behavior of adsorbing electrolyte.

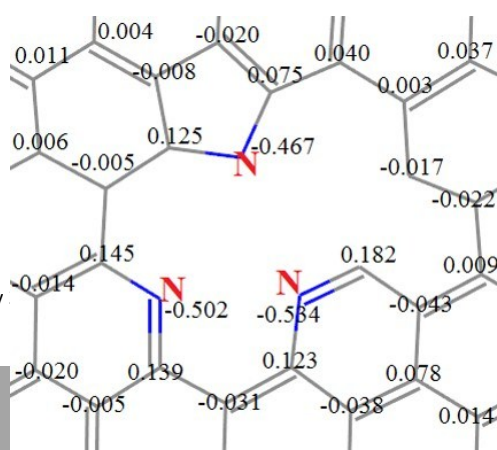


Figure S9 DFT calculation of the charge distribution of PC/RGO after N-doping.

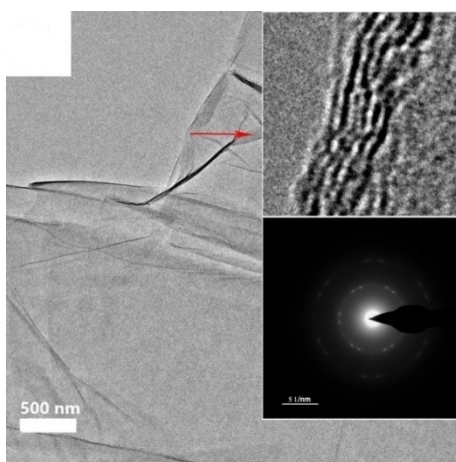


Figure S10 TEM image of GO. As shown in the enlarged image of GO edge (upper inset), it is less than 10 layers. Also, the SAED results present typical patterns of GO (inset below).

Table S1. Chemical compositions of $\text{Co}_x\text{S}@PC/\text{RGO}$ and PC/RGO .

$\text{Co}_x\text{S}@PC/\text{RGO}$	wt%	at%	PC/RGO	wt%	at%
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C	10.55	27.65	C	90.23	93.07
N	1.87	4.21	N	4.33	3.83
O	5.26	10.36	O	3.53	2.74
S	30.77	30.23	Zn	1.91	0.36
Co	51.55	27.55			

Table S2. Cycling performances of cobalt sulfides for ECs.

Sample	Electrolyte	Current density	Capacitance retention	Ref.
CoS/Graphene	1 M KOH	1 A g ⁻¹	94.8 % (2000 cycles)	6
CoS/Graphene	2 M KOH	10 A g ⁻¹	< 50 % (2500 cycles)	14
Flower-like CoS	6 M KOH	3 A g ⁻¹	91 % (1000 cycles)	29
CoS nanocages	1 M KOH	10 A g ⁻¹	88.2 % (1000 cycles)	32
Co _x S@PC/RGO	1 M KOH	1 A g ⁻¹	99.7 % (4000 cycles)	This work

Table S3. Cycling performances of HECs

HEC	Electrolyte	Current density	Capacitance retention	Ref.
graphene/MnO ₂ //ACN	1 M Na ₂ SO ₄		97.2 % (1000 cycles)	33
β-Ni(OH) ₂ // AC	6 M KOH	5 mA cm ⁻²	92 % (1000 cycles)	40
NiCo ₂ S ₄ // AC	6 M KOH	5 mA cm ⁻²	76.5 % (5000 cycles)	41
RuO ₂ /graphene // graphene	3 M NaOH	1 A g ⁻¹	95 % (2000 cycles)	46
graphene/MnO ₂ // graphene	1 M Na ₂ SO ₄	0.5 A g ⁻¹	79 % (1000 cycles)	47
MnO ₂ // FeOOH	5 M LiCl		95.9 % (5000 cycles)	48
FeOOH//Co-Ni double hydroxides	3 M KOH		92.3 % (3000 cycles)	49
Co _x S@PC/RGO//PC/RGO	1 M KOH	2 A g ⁻¹	100 % (2000 cycles)	This work

Supplementary Notes

Note S1. Synthesis of optimized Co_xS@PC/RGO.

Cobalt sulfide was obtained through a synergic process, in which decomposition and sulfidation happened simultaneously. In details, Co ions within ZIF-67 nanoparticles were converted to cobalt sulfide nanocrystals while organic ligands were carbonized to porous carbon, forming core-shell units.

ZIF-67/GO precursor was mixed with sulfur powder and annealed under nitrogen atmosphere at 500, 550, 600, 650 and 700 °C in a weight ratio of 2: 1 (donated as Sample-T, T= temperature, e.g. Sample-500). XRD patterns reveal that all samples could be assigned to Co₉S₈ (JCPDS: 19-0364) except for Sample-500 (Figure S1a), in which some impure peaks were observed. Also, the characteristic peaks become sharper with increasing temperature, indicating higher crystallinity.

Also, effects of the molar ratio of ZIF-67: S were studied by keeping the same amount of ZIF-67/GO (0.12 g) while changing the amount of sulfur powders (from 0.04, 0.06, to 0.12 g, which correspond to molar ratios from 1: 2.6, 1: 3.4, to 1: 7.8, respectively). XRD patterns reveal that ZIF-67 was converted to cobalt sulfide in all cases. Specially, the sample obtained in the weight ratio of 1: 1 shows impure peaks that could be indexed to Co₄S₃ phase (JCPDS: 02-1458). Therefore, in order to provide excessive sulfur powder and get pure Co₉S₈, 650 °C and the weight ratio of 2:1 were chosen as optimized annealing parameters.

Note S2. Electrochemical impedance spectrometry discussion.

As shown in Figure 5b and Figure S4, for all samples, their Nyquist plots show semicircles in high frequency region and then transform from near 45 ° lines to vertical lines with decreasing frequency.

The overall resistance of an electrode (resistance at the “knee” point, R_{knee}) can be determined by the extrapolation of the capacitive line to the 45 ° line (Figure 5b).⁵⁰ The relationship between various resistances follows the equations below.

$$R_{knee} = R_{\Omega} + R_p + R_D \quad (S1)$$

$$R_{\Omega} = R_A + R_B + R_C \quad (S2)$$

The internal resistance of an electrode (notated as R_{Ω} or R_{ESR}), i.e. the point intersecting with real axis at high frequency, includes ionic resistance of electrolyte (R_A), intrinsic resistance of electrode materials (R_B) and contact resistance (R_C , negligible due to the high conductivity of nickel mesh).⁵¹ The polarization resistance (R_p), i.e. the diameter of semicircle, reveals penetrating ability of electrolyte into porous electrode. The diffusional resistance (R_D), i.e. the length of 45 ° line in middle frequency region, indicates migration rate of ions from electrolyte inside pores to the surface of electrode. Clearly, the PC/RGO electrode presents smaller R_{ESR} than that of the PC one either at the initial state or after 5000 cycles, demonstrating that electronic conductivity is effectively improved after the introduction of RGO. Also, R_p of PC/RGO with pore size of 3.98 nm is smaller than that of PC with pore size of less than 2 nm, indicating easier ion diffusion into larger pores. In addition, the short 45 ° line for PC/RGO also reveals smooth ion diffusion inside larger pores.

Besides resistances, the straight line in low frequency region is an important measurement of capacitive behavior. For instance, a vertical line suggests ideal capacitive performance.⁵² At the initial state, both the PC and PC/RGO electrodes show ideal capacitive behaviors. In addition, the PC/RGO electrode still maintains excellent capacitive behavior after 5000 cycles. However, that for the PC electrode gets worse, which might be caused by distortion and agglomeration of individual nanoparticles. Figure S6b shows the original relationship between the real part (Z_{Re}) of total resistance and frequency. Z_{Re} can be calculated according to a simplified equation when frequency approaches zero:⁵³

$$Z_{Re} = R_{\Omega} + R_{ct} + \sigma\omega^{-\frac{1}{2}} \quad (S3)$$

where R_{Ω} is the resistance of electrolyte (Ω), R_{ct} is charge transfer resistance (Ω), σ is Warburg coefficient ($\Omega \text{ rad}^{1/2} \text{ s}^{-1/2}$), and ω is angular frequency (rad s^{-1}). According to the slopes of fitted lines, Warburg coefficients are 2.2 and 3.1 $\Omega \text{ rad}^{1/2} \text{ s}^{-1/2}$ for PC electrode before and after 5000 cycles, indicating its performance decline after cycling. For PC/RGO, its Warburg coefficient is 1.96 $\Omega \text{ rad}^{1/2} \text{ s}^{-1/2}$ before cycling. It is noteworthy that it decreases to 1.04 $\Omega \text{ rad}^{1/2} \text{ s}^{-1/2}$ after 5000 cycles, revealing its superior capacitive property after activation.

Accordingly, our sandwich-like PC/RGO naturally satisfies three requirements of electrode materials: (i) high electronic conductivity induced by RGO substrate, (ii) fast ion transport pathways provided by sufficient and proper pores, and (iii) stable structure that neither agglomerates nor restacks during longtime cycling.

Supplementary References

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