Electronic Supporting Information (ESI)

Designing a Carbon Nanotubes Interconnected ZIF-derived Cobalt Sulfide Hybrid Nanocage for Supercapacitors

Siou-Ling Jian,^{*a*,§} Li-Yin Hsiao,^{*a*,§} Min-Hsin Yeh,^{*b*}* and Kuo-Chuan Ho^{*a*,*c*,*d*}*

^a Department of Chemical Engineering, National Taiwan University, Taipei 10617, Taiwan

^b Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei 10607, Taiwan

^c Institute of Polymer Science and Engineering, National Taiwan University, Taipei 10617, Taiwan

^d Advanced Research Center for Green Materials Science and Technology, National Taiwan University,

Taipei 10617, Taiwan

[§] *The authors contributed equally to this work.*

Table S1 A list of ^{*a*} MOF-derived cobalt sulfide and ^{*b*} carbon/cobalt sulfide materials in the application of supercapacitors, compared to that obtained in this work. ^{*c*} Co₉S₈ embedded in carbon co-doped with N and S. ^{*d*} Co₉S₈@S, N-doped carbon cuboid. ^{*e*} CoS-nanoparticle-assembled nanoboxes surrounded by outer CoS-nanosheetconstructed shells. ^{*f*} Co_xS@porous carbon/RGO. ^{*g*} conductive polymer/rGO/Co₉S₈.

Materials	Electrolyte	Gravimetric capacitance (F g ⁻¹) (Potential range <i>vs</i> . Hg/HgO)	Capacitance retention	Ref.
Co ₉ S ₈ -nanosheet array ^{<i>a</i>}	1.0 M KOH	1,098.8 (0.15 – 0.55 V, 0.5 A g ⁻¹)	1,000 (87.4%)	1
CoS nanocages ^a	1.0 M KOH	1,475 (-0.15 – 0.35 V, 1 A g ⁻¹)	3,000 (70.3%)	2
C09S8/NS-C <i>a, b, c</i>	6.0 M KOH	734.09 (0 – 0.5 V, 1 A g ⁻¹)	140,000 (99.8%)	3
Co ₉ S ₈ @SNCC <i>a</i> , <i>b</i> , <i>d</i>	6 M KOH	429 (-1.1 – -0.6V, 1 A g ⁻¹)	2,000 (98%)	4
Zn-Co-S ^a	6.0 M KOH	1,266 (0.15 – 0.65 V, 1 A g ⁻¹)	10,000 (91%)	5
CoS-NP/CoS-NS ^{a,} e	2.0 M KOH	980 (0.15 – 0.70 V, 1 A g ⁻¹)	10,000 (89%)	6
CoS-N-doped carbon ^{<i>a</i>, <i>b</i>}	2.0 M KOH	360.1 (0.1 – 0.7 V, 1.5 A g ⁻¹)	2,000 (90%)	7
Co_xS@PC/RGO <i>a</i> , <i>b</i> , <i>f</i>	1.0 M KOH	455 (0.15 – 0.65 V, 2 A g ⁻¹)	4,000 (99.7%)	8
CoS _x /FMWCNTs ^b	2.0 M KOH	334 (-0.15 – 0.60 V, 0.4 A g ⁻¹)	1,000 (95%)	9
CNT/CoS ^b	1.0 M KOH	1,332.8 (0.15 – 0.65 V, 217.4 A g ⁻¹)	1,500 (91%)	10
CoS/CNT ^b	6.0 M KOH	804 (0.15– 0.65 V, 0.5 A g ⁻¹)	1,000 (93.4%)	11

rGO ₁₀₀ -CNT ₅₀ - Co ₃ S ₄ ^b	6.0 M KOH	977 (0.15 – 0.65 V, 1 A g ⁻¹)	3,000 (90%)	12
RGO/CoS ^b	6.0 M KOH	1,130 (0.15 – 0.65 V, 0.5 A g ⁻¹)	1,000 (92.1%)	13
cP/rGO/Co ₉ S ₈ ^{b,g}	2.0 M KOH	788.9 (0.1 – 0.55 V, 1 A g ⁻¹)	10,000 (over 100%)	14
CoS@rGO ^b	2.0 M KOH	849 (0 – 0.55 V, 5 mA cm ⁻²)	3,000 (90.5%)	15
Co ₃ S ₄ /rGO ^b	2.0 M KOH	675.9 (0 – 0.5 V, 0.5 A g ⁻¹)	1,000 (over 100%)	16
CoS/rGO ^b	6.0 M KOH	550 (0.15 – 0.55 V, 1A g ⁻¹)	5,000 (95%)	17
Co ₃ S ₄ -rGO ^b	2.0 M KOH	2314 (-0.15 – 0.75 V, 2 mV/s)	1,000 (92.6%)	18
Co ₉ S ₈ /reduced graphene ^b	6.0 M KOH	728 (0.15 – 1.15 V, 2 A g ⁻¹)	1,000 (97%)	19
Co ₉ S ₈ /RGO ^b	6.0 M KOH	616 (0 – 0.8 V, 4.4 A g ⁻¹)	1,000 (98%)	20
PANI-rGO-CoS ^b	1.0 M H ₂ SO ₄	431 (0.15 – 0.95 V, 0.5A g ⁻¹)	1,000 (90.1%)	21
CoS/graphene ^b	2.0 M KOH	3,386 (0.05– 0.55 V, 1 A g ⁻¹)	2,500 (31.1%)	22
CoS/graphene ^b	6.0 M KOH	564 (0.1 – 0.55 V, 1 A g ⁻¹)	2,000 (94.8%)	23
CoS/graphene ^b	6.0 M KOH	2,423.3 (-0.7 – 0.1 V, 5 mV/s)	-	24
Co ₉ S ₈ /3D graphene	1.0 M KOH	2,317 (0.1 – 0.55 V, 1 A g ⁻¹)	6,000 (90%)	25
3D graphene/CoS _x ^b	1.0 M KOH	443 (0 – 0.6 V, 1 A g ⁻¹)	5,000 (86%)	26

Co ₃ S ₄ -N-doped graphene ^b	6.0 M KOH	2,245 (0.05– 0.3 V, 3 A g ⁻¹)	-	27
g-C ₃ N ₄ /CoS ^b	3.0 M KOH	668 (0.15 – 0.55 V, 2 A g ⁻¹)	1,000 (98%)	28
Hybrid CNT/CoS nanocage ^{a, b}	6.0 M KOH	2,173.1 (0.08 – 0.48 V, 5 A g ⁻¹)	1,000 (91.1%)	This work

Table S2 A list of asymmetric supercapacitor ^a and symmetric supercapacitor ^b composed of cobalt sulfide as the electrode (AC=Activated carbon; rGO=reduced graphene oxide).

Electrodes	Electrolyte	Energy density (Wh kg ⁻¹)/ Power density (W kg ⁻¹)	Capacitance retention	Ref.
Co ₃ S ₄ //Co ₃ S ₄ -rGO ^{<i>a</i>}	PVA/KOH	1.09/398 & 0.31/750 (0 – 1.5 V)	5,000 (89.56%)	18
CoS@eRG//AC a	2 М КОН	29/800 & 11/4,000 (0 – 1.6 V)	3,000 (70.3%)	22
Co ₉ S ₈ nanoflakes//AC ^a	6 M KOH	31.4/2,000 & 26.3/4,000 (0 – 1.6 V)	5,000 (89.5%)	29
Co ₉ S ₈ //rGO ^a	6 M KOH	68.6/1,319 (0 – 1.2 V)	1,000 (96%)	30
CNT/CoS nanocage ^b	6 М КОН	62.4/674.6 & 23.3/3,382.2 (0 – 1.35 V)	5,000 (96.6%)	This work



Figure S1 CNT dispersed in methanol with (left) and without (right) PVP.



Figure S2 FE-SEM images of ZIF-67 nanoparticles synthesized with PVP.



Figure S3 Particle size distributions of (a) CNT/ZIF-67 1:1, (b) CNT/ZIF-67 1:2, and (c) CNT/ZIF-67 1:8.



Figure S4 FE-SEM images of CNT/ZIF-67 composites with unfunctionalized CNTs.



Figure S5 FE-SEM images of (a) ZIF-67 nanoparticles, and (b) CoS nanocages.



Figure S6 Particle size distributions of (a) CoS, (b) CNT/CoS 1:2 and (c) CNT/CoS 1:8.



Figure S7 FE-SEM images of CNT/ZIF-67 1:1, CNT/CoS 1:1 and the schematic illustration of the collapsed CoS *via* sulfurization.



Figure S8 XRD patterns of CoS cage and hybrid CNT/CoS nanocages with various sizes of ZIF-67 as templates.



Figure S9 CVs of (a) CoS nanocage, (b) CNT/CoS 1:1 nanocage, (c) CNT/CoS 1:8 nanocage, and (d) CNT/CoS mixture electrodes at different scan rates.



Figure S10 GCD curves of (a) CoS nanocage, (b) CNT/CoS 1:1 nanocage, (c) CNT/CoS 1:8 nanocage, and (d) CNT/CoS mixture electrodes at different current densities.



Figure S11 Electrochemical active surface area using CVs recorded in non-faradic region at different scan rates. (a) Linear fits of anodic current density measured at 0.95 V (*vs.* RHE) versus scan rate plots. (b) CNT/CoS 1:1 nanocage, (c) CNT/CoS 1:2 nanocage and (d) CNT/CoS 1:8 nanocage.



Figure S12 (a) Cycling performance of hybrid CNT/CoS nanocage and CNT/CoS mixture, and (b) Ragone plot of CoS nanocage, hybrid CNT/CoS nanocage and CNT/CoS mixture under various current densities in three-electrode system.



Figure S13 A photograph of the symmetric supercapacitor of hybrid CNT/CoS nanocage as electrodes.

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