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Zeolitic imidazolate framework-67-derived chalcogenides as electrode materials for supercapacitors†

Lidong Jiao,^a Mingshu Zhao,^a  [✉] Qingyang Zheng,^b Qingyi Ren,^a Zhou Su,^a Min Li^a and Feng Li^a

With the rapid development of new energy technologies, hybrid supercapacitors have received widespread attention owing to their advantages of high power density, fast charging/discharging rate and long cycle life. In this case, the selection and design of electrode materials are the key to improving the energy storage performance of supercapacitors. Herein, zeolitic imidazolate framework-67 (ZIF-67) is presented as a good candidate material for the fabrication of supercapacitor electrodes because of its controllable pore size, constant cavity size and large specific area. Moreover, pristine ZIF-67 and ZIF-67-derived porous carbon have shown exemplary performances in supercapacitors. However, they belong to the class of electric double layer capacitor materials and have a lower magnitude of energy storage compared with pseudocapacitor materials. Therefore, to improve the energy density of hybrid supercapacitors, other ZIF-67 derivatives need to be explored, especially chalcogenides. This review mainly reports the application of ZIF-67-derived transition metal chalcogenides (TMCs, C including Oxide, Sulfide, Selenide, Telluride) in supercapacitors. Moreover, the strategies for the preparation of ZIF-67-derived TMCs and their electrochemical performance in supercapacitors are further discussed. Finally, the remaining challenges and future perspectives are highlighted.

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1. Introduction

With the continuous development of society and the economy, energy storage has become a key element in achieving energy sustainability goals, leading to energy and cost savings.^{1–3} Thus, supercapacitors have attracted widespread attention from scientific researchers owing to their advantages of high power density, fast charging/discharging rate and long cycle life.^{4–9} However, their relatively low energy density limits their further practical application.^{10–12} Therefore, increasing research has been conducted on hybrid supercapacitors because of their charge-storage mechanisms, including both electric double layer capacitance and pseudocapacitance, resulting in better cycling stability than pseudocapacitors and higher energy density than electric double layer capacitors (EDLCs).^{13–18} Moreover, there has been growing demand for

both high energy and high power densities in the same material.^{19–23}

As a new class of porous crystal materials, metal organic frameworks (MOFs), which are composed of organic ligands and metal cations linked *via* coordination bonds, have been widely studied in the field of nanotechnology and energy storage because of their inherent advantages such as abundant porosity, high specific surface area and controllable topology.^{24–26} Moreover, with the development of various synthetic strategies, many new MOFs with a specific topology or architecture have been manufactured and applied as supercapacitor electrode materials.^{27,28} In recent years, an increasing number of MOFs have been used as templates or precursors to generate MOF derivatives, such as porous carbon,²⁹ metal-doped carbon, hydroxides, phosphides³⁰ and chalcogenides (O,³¹ S,³² Se,³³ and Te³⁴). Furthermore, it has been proven that the size, shape and composition of MOF derivatives can be effectively controlled on the basis of their precursors.^{35,36} Moreover, various conductive matrices (conductive polymers,³⁷ carbon-based materials^{38,39} and MXene materials^{40,41}) have been combined with pristine MOFs or MOF derivatives to improve their conductivity and structural stability during long-term cycling, resulting in promising cycling stability, better rate performance and high specific

^aSchool of Physics, Key Laboratory of Shaanxi for Advanced Functional Materials and Mesoscopic Physics, MOE Key Laboratory for Non-equilibrium Synthesis and Modulation of Condensed Matter, Xi'an Jiaotong University, Xi'an, 710049 Shaanxi, China. E-mail: zhaomshu@mail.xjtu.edu.cn; Tel: +86-13186193932

^bXi'an High-tech Research Institute, 710025 Xi'an, China

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capacitance/capacity.³⁴ However, some of these MOFs are unstable in water and alkaline solutions, which limit their use in supercapacitors.⁴²

As a member of metal–organic frameworks, zeolitic imidazolate framework-67 (ZIF-67) is a good candidate material for the fabrication of supercapacitors (as shown in Fig. S1†) because of its controllable pore size, high chemical stability and thermal stability.^{43,44} The ZIF-67 material (as shown in Fig. 1) is composed of imidazole and Co^{2+} , which can provide a large specific area and abundant oxidation active sites as an electrode material precursor, together with a constant cavity and thermal stability.⁴⁵ Thus, ZIF-67 has been considered as a promising electrode material for supercapacitors. For example, Xie *et al.*⁴⁶ successfully prepared one-dimensional ZIF-67, which exhibited a much higher charge storage capacity, rate capability and cycling stability than two-dimensional and three-dimensional ZIF-67 because of its abundant linker-missing defects and favorable exposure of cobalt ions as redox active sites. Moreover, due to the drawback of low conductivity of pristine ZIF-67, ZIF-67-derived porous carbon materials are also considered good EDLC materials for supercapacitors. Torad *et al.*⁴⁷ synthesized nanoporous carbon *via* the one-step direct carbonization of ZIF-67, which showed a good electrochemical performance of 238 F g^{-1} at 20 mV s^{-1} in $0.5 \text{ M H}_2\text{SO}_4$ electrolyte. However, both pristine ZIF-67 (Table S1†) and ZIF-67-derived porous carbon (Table S2†) have a low energy density because they are EDLC materials. Therefore, it is necessary to develop new ZIF-67-derived pseudocapacitors materials to improve the energy density of hybrid supercapacitors.

As typical pseudocapacitor materials, transition metal chalcogenides (TMCs, C including O, S, Se, and Te) have been widely researched and applied in hybrid supercapacitors, exhibiting both high energy density and power density.³⁴ Thus, in this review, we focus on ZIF-67-derived TMCs as electrode

materials for application in supercapacitors. With the development of single-metal compounds to multi-metal compounds and composite materials, their preparation technology and electrochemical performances in supercapacitors are discussed to highlight the relevant challenges that need to be resolved in the future, enabling the research and development of high-performance materials. Furthermore, significantly, this review can guide the direction of future work based on the comparison of the electrochemical performance of various derivatives in supercapacitors.

2. ZIF-67-derived transition metal oxides

Metal oxide materials derived from ZIF-67 possess a high reversible capacity and superior rate and cycle performance, making them excellent electrode materials²⁵ (as shown in Table 1), which can be easily obtained by thermal treatment, while their charge storage mechanisms obey pseudocapacitance behavior.⁴⁸ Moreover, in the future, the class of transition metal oxides will play a crucial role in the development of cost-effective, high-powered, and environment-friendly energy storage.²

2.1 Single metal oxides

Salunkhe *et al.*⁴⁹ prepared both nanoporous carbon and nanoporous cobalt oxide materials from a single ZIF-67 precursor by optimizing the annealing conditions, as shown in Fig. 2a. The resulting ZIF-derived carbon possessed highly graphitic walls and a high specific surface area of $350 \text{ m}^2 \text{ g}^{-1}$, while the resulting ZIF-derived nanoporous Co_3O_4 possessed a high specific area of $148 \text{ m}^2 \text{ g}^{-1}$. Also, when both materials were tested in a three-electrode system, they showed high capacitance values (272 and 504 F g^{-1} , respectively, at a scan rate of 5 mV s^{-1}). Also, Zhang *et al.*⁵⁰ successfully constructed a supercapacitor by adopting porous hollow Co_3O_4 derived from the ZIF-67 rhombic dodecahedral structure as the electrode material, which showed a large specific capacitance of 1100 F g^{-1} and retained more than 95.1% of its specific capacitance after 6000 continuous charge–discharge cycles. Meanwhile, Guo *et al.*⁵⁸ reported an effective approach to synthesize cohesive porous $\text{Co}_3\text{O}_4/\text{C}$ materials using a ZIF-67 single-source precursor *via* two-step calcination. As a supercapacitor electrode material, the $\text{Co}_3\text{O}_4/\text{C}$ composite exhibited a higher specific capacitance (875.6 F g^{-1} at 1 A g^{-1}) and better cycling stability (capacitance retention of 87.8% after 1000 cycles at 6 A g^{-1}) compared to pure Co_3O_4 (245.3 F g^{-1} and 78.4% under the same conditions). In addition, it showed good cycling stability with a capacitance retention of 82% after 1000 cycles at 6 A g^{-1} in a symmetric supercapacitor device. The better electrochemical performance of the composite can be attributed to the improvement in conductivity, larger surface area for more active sites, and the ameliorative volume expansion of Co_3O_4 by the stable structure of Co_3O_4 nanoparticles well embedded in the partially graphitized carbon matrix during the long

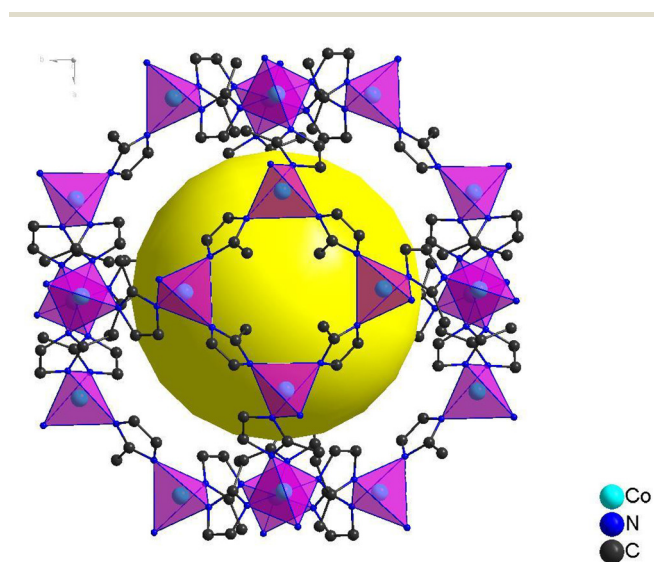


Fig. 1 Schematic of the structure of ZIF-67, showing the connection between its various atoms.

Table 1 Summary of the electrochemical characteristics of ZIF-67-derived oxide materials determined using three-electrode measurements

Electrode materials	Specific capacity	Electrolyte	Potential window (CV)	Capacity retention	Cyclic stability	Ref.
Co ₃ O ₄	504 F g ⁻¹ at 5 mV s ⁻¹	6 M KOH	−0.1–0.4 V (Ag/AgCl)	52% (5 to 200 mV s ⁻¹)		49
Co ₃ O ₄	1110 F g ⁻¹ at 1.25 A g ⁻¹	3 M KOH	0–0.5 V (Hg/HgO)	39.4% (1.25 to 12.5 A g ⁻¹)	95.1% (6000)	50
Co ₃ O ₄ -NTA	2.26 C cm ⁻² at 2 mA cm ⁻²	2 M KOH	0–0.6 V	46.9% (2 to 40 mA cm ⁻²)	96.9% (5000)	51
Co ₃ O ₄ /3DGN/NF	321 F g ⁻¹ at 1 A g ⁻¹	6 M KOH	0–0.5 V (Hg/HgO)	76.6% (1 to 20 A g ⁻¹)	88% (2000)	52
Co ₃ O ₄ /C@MoS ₂	1076 F g ⁻¹ at 1 A g ⁻¹	2 M KOH	0–0.7 V (Ag/AgCl)	76.9% (1 to 10 A g ⁻¹)	64.5% (5000)	53
Co ₃ O ₄ -CeO ₂	1288.3 F g ⁻¹ at 2.5 A g ⁻¹	3 M KOH	0–0.55 V (Hg/HgO)	53.3% (2.5 to 12.5 A g ⁻¹)	>96.7% (6000)	54
M-Co ₃ O ₄	1216.4 F g ⁻¹ at 1 A g ⁻¹	2 M KOH	0–0.6 V (Hg/HgO)	76.1% (1 to 20 A g ⁻¹)		55
Ni _x Co _{3-x} O ₄ /CNTs	668 F g ⁻¹ at 1 A g ⁻¹	2 M KOH	0–0.6 V (Ag/AgCl)	91.6% (1 to 10 A g ⁻¹)	91.2% (2000)	56
MnCo ₂ O ₄ @Co ₃ O ₄	1440 C cm ⁻² at 1 mA cm ⁻²	2 M KOH	0–0.6 V (SCE)	36% (1 to 10 mA cm ⁻²)	82.76% (8000)	57
Co ₃ O ₄ /C	875.6 F g ⁻¹ at 1 A g ⁻¹	6 M KOH	0–0.5 V (Ag/AgCl)		87.8% (1000)	58
Co ₃ O ₄ @N-pC	422.8 F g ⁻¹ at 1 A g ⁻¹	1 M KOH	−0.2–0.8 V (SCE)	60.5% (1 to 5 A g ⁻¹)	87.9% (5000)	59
rGO/Co ₃ O ₄	688 F g ⁻¹ at 1 A g ⁻¹	6 M KOH	0–0.5 V (SCE)	64.3% (1 to 10 A g ⁻¹)	79.7% (1000)	60
Co ₃ O ₄ /Co(OH) ₂	184.9 mA h g ⁻¹ at 1 A g ⁻¹	1 M KOH	−0.1–0.4 V (Ag/AgCl)	76% (1 to 16 A g ⁻¹)		61
Co ₃ O ₄ /MCS	1409.5 F g ⁻¹ at 0.5 A g ⁻¹	1 M KOH	0–0.65 V (SCE)	93.5% (0.5 to 1 A g ⁻¹)	93.2% (1000)	62
Au@Co ₃ O ₄	763 F g ⁻¹ at 1 A g ⁻¹	2 M KOH	0.2–0.7 V	76% (1 to 10 A g ⁻¹)	83.7% (5000)	63
ZCCO	701 C g ⁻¹ at 2 A g ⁻¹	3 M KOH	−0.1–0.55 V (Hg/HgO)	61% (2 to 60 A g ⁻¹)	93.6% (6000)	64
NiCo LDH/Co ₃ O ₄	1393.9 F g ⁻¹ at 1 A g ⁻¹	3 M KOH	0–0.5 V (Ag/AgCl)	71.3% (1 to 15 A g ⁻¹)	88.4% (5000)	65
NS-Co ₃ O ₄ @PC	940 F g ⁻¹ at 1 A g ⁻¹	6 M KOH	0–0.6 V (Hg/HgO)	42.5% (1 to 20 A g ⁻¹)		66
Co ₃ O ₄ @MnO ₂	413 F g ⁻¹ at 0.5 A g ⁻¹	1 M LiOH	0–0.6 V (Ag/AgCl)	41% (0.5 to 10 A g ⁻¹)	110% (2000)	67
NiMoO ₄ @Co ₃ O ₄ /CA	436.9 C g ⁻¹ at 0.5 A g ⁻¹	2 M KOH	0–0.6 V (SCE)	70.7% (0.5 to 10 A g ⁻¹)	82.7% (5000)	68
3D-H CoWO ₄ /NF	1395 F g ⁻¹ at 0.5 A g ⁻¹	6 M KOH	0–0.6 V (SCE)	32.3% (0.5 to 40 A g ⁻¹)	89% (3000)	69
Co ₃ V ₂ O ₇ /G	276.5 C g ⁻¹ at 1 A g ⁻¹	1 M KOH	0–0.6 V (Ag/AgCl)	62.5% (1 to 20 A g ⁻¹)	93% (10 000)	70
Z-CoO/RGO	275 F g ⁻¹ at 1 A g ⁻¹	6 M KOH	−1–0 V (Ag/AgCl)	53% (1 to 10 A g ⁻¹)		71
Fe-doped Co ₃ O ₄	1535.8 F g ⁻¹ at 1 A g ⁻¹	6 M KOH	0–0.5 V (Hg/HgO)		88% (8000)	72
Co ₃ O ₄ /NiCo ₂ O ₄	770 F g ⁻¹ at 1 A g ⁻¹	6 M KOH	0–0.5 V (Ag/AgCl)	84% (1 to 20 A g ⁻¹)	70% (10 000)	73
Co ₃ O ₄ /NiNH	583 C g ⁻¹ at 1 A g ⁻¹	6 M KOH	0–0.6 V (Hg/HgO)	82% (1 to 20 A g ⁻¹)		74
Co ₃ O ₄ /N-rGA	1485 F g ⁻¹ at 1 A g ⁻¹	6 M KOH	0–0.4 V (SCE)	61% (1 to 20 A g ⁻¹)	93.4% (5000)	75
NPC-60	594.8 mF cm ⁻² at 5 mV s ⁻¹	6 M KOH	0–0.45 V (SCE)		64% (2000)	76
Co ₃ O ₄ @C	703.3 F g ⁻¹ at 1 A g ⁻¹	1 M KOH	0–0.8 V (SCE)	82.7% (1 to 10 A g ⁻¹)	100% (10 000)	77
ZnO/Co ₃ O ₄ /NiO	1119.11 C g ⁻¹ at 1 A g ⁻¹	2 M KOH	−0.1–0.7 V (SCE)	72.92% (1 to 10 A g ⁻¹)	93.75% (5000)	78
Co ₃ O ₄ @Co/NC-HN	273.9 mA h g ⁻¹ at 1 A g ⁻¹	3 M KOH	0–0.75 V (Hg/HgO)	47.6% (1 to 10 A g ⁻¹)	86.3% (3000)	79
Co ₃ O ₄ @NPC/Ni	525 F g ⁻¹ at 1.5 A g ⁻¹	1 M KOH	0–0.6 V (Ag/AgCl)	42.9% (1.5 to 5 A g ⁻¹)	81% (8000)	80
Porous Co ₃ O ₄ -CNTs	875 F g ⁻¹ at 5 mV s ⁻¹	6 M KOH	0–0.5 V (SCE)		98% (1000)	38
CoO _x /carbon	1660.4 F g ⁻¹ at 1 A g ⁻¹	1 M KOH	−0.1–0.4 V (Ag/AgCl)	22% (1 to 20 A g ⁻¹)	95.9% (10 000)	81
Co ₃ O ₄ @NiO	1017 F g ⁻¹ at 1 A g ⁻¹		0–0.6 V (SCE)	55.9% (1 to 25 A g ⁻¹)	90.1% (10 000)	82
Co ₃ O ₄ HPCs	140 F g ⁻¹ at 1 A g ⁻¹		0–0.5 V (Hg/HgO)	49.5% (1 to 15 A g ⁻¹)		83
Co ₃ O ₄ @N-doped C	709 F g ⁻¹ at 1 A g ⁻¹	1 M KOH	0–0.4 V (Ag/AgCl)	43% (1 to 10 A g ⁻¹)	83% (5000)	84
α-Ni(Co)S@NiCoO ₂	502.4 mA h g ⁻¹ at 1 A g ⁻¹	2 M KOH	−0.2–0.7 V (Ag/AgCl)	45.7% (1 to 20 A g ⁻¹)		85
Co-O-NSs@CFC	842 F g ⁻¹ at 1 A g ⁻¹	6 M KOH	0–0.6 V (Ag/AgCl)	40% (1 to 20 A g ⁻¹)	96.4% (10 000)	86
CoVO-HNC	427.64 F g ⁻¹ at 1 A g ⁻¹	3 M KOH	0–0.6 V (Hg/HgO)	88% (1 to 10 A g ⁻¹)	89.38% (10 000)	87
Co ₃ O ₄ @CoNi ₂ S ₄ -20/CC	1798 F g ⁻¹ at 1 A g ⁻¹	1 M KOH	0–0.6 V (Ag/AgCl)	77.9% (1 to 10 A g ⁻¹)		88
Ni-Co LDH@Co ₃ O ₄ NC	1866 F g ⁻¹ at 2 A g ⁻¹	1 M KOH	0–0.6 V (Ag/AgCl)	80% (2 to 40 A g ⁻¹)		89
Co ₃ O ₄ @C	251 F g ⁻¹ at 1 A g ⁻¹	1 M KOH	0–0.6 V (Hg/HgO)	84% (1 to 5 A g ⁻¹)	90% (5000)	90
NiCo ₂ O ₄ /graphene	1365 F g ⁻¹ at 1 A g ⁻¹	1 M KOH	0–0.65 V (Ag/AgCl)	51.5% (1 to 10 A g ⁻¹)	89.11% (2000)	91
Ni/Co-CN	1701 F g ⁻¹ at 1 A g ⁻¹	3 M KOH	0–0.5 V (Ag/AgCl)	61.9% (1 to 10 A g ⁻¹)		92
Co ₃ O ₄ @MnO ₂	768 C g ⁻¹ at 1 A g ⁻¹	1 M KOH	0–0.6 V (Hg/HgO)		86% (5000)	93
Co(OH)F@Co ₃ O ₄ /NF	543 F g ⁻¹ at 1 A g ⁻¹	3 M KOH	0–0.7 V	57.8% (1 to 10 A g ⁻¹)	88.34% (5000)	94
Co ₃ O ₄ @NC	1144 F g ⁻¹ at 1 A g ⁻¹	6 M KOH	0–0.6 V (Hg/HgO)	45.4% (1 to 20 A g ⁻¹)	91.6% (10 000)	95
CoMoO ₄ @Co ₃ O ₄	2003 F g ⁻¹ at 1 A g ⁻¹	3 M KOH	−0.1–0.6 V (Ag/AgCl)		68% (5000)	96
Co ₃ O ₄ @SiO ₂ /PPy	107.7 F g ⁻¹ at 0.6 A g ⁻¹	1 M KOH	−0.55–0.45 V (Ag/AgCl)			97
MWCNT _x @Co ₃ O ₄	206.89 F g ⁻¹ at 1 A g ⁻¹	3 M KOH	0–0.6 V (Ag/AgCl)	92.6% (1 to 5 A g ⁻¹)	78.9% (1000)	98
HCT-2@Co ₃ O ₄ @SnS ₂	439 F g ⁻¹ at 1 A g ⁻¹	6 M KOH	0–0.5 V (Hg/HgO)	72.1% (1 to 20 A g ⁻¹)	63.5% (15 000)	99
Co ₃ O ₄ -VG-CC	1360 F g ⁻¹ at 2.5 A g ⁻¹	2 M KOH	0–0.8 V (Hg/HgO)	90% (2.5 to 50 A g ⁻¹)		100
Co ₃ O ₄ /NiCo ₂ O ₄ DSNCs	236.18 C g ⁻¹ at 1 mA cm ⁻²	2 M KOH	0–0.6 V (SCE)	63.1% (1 to 20 mA cm ⁻²)	103.43% (5000)	101
Carbon/TiO ₂ /Co ₃ O ₄	481.7 F g ⁻¹ at 1 A g ⁻¹	3 M KOH	−0.05–0.55 V (Hg/HgO)	78.9% (1 to 10 A g ⁻¹)	91.6% (10 000)	102
Co ₃ O ₄ -NiCo ₂ O ₄ @CF	166.25 F g ⁻¹ at 1 A g ⁻¹	1 M KOH	−0.5–0.5 V (Ag/AgCl)	91% (1 to 2.5 A g ⁻¹)		103
CoO _x /CNF	750 mF cm ⁻² at 10 mV s ⁻¹	6 M KOH	0–1 V	81% (10 to 100 mV s ⁻¹)	91% (10 000)	104
NM-CH/ZnO@Co ₃ O ₄ CNCs	1179 F g ⁻¹ at 0.5 A g ⁻¹	1 M KOH	0–0.7 V (Ag/AgCl)	72.5% (0.5 to 20 A g ⁻¹)	98% (25 000)	105
CoFe ₂ O ₄ -Fe@NC-700	3960.9 F g ⁻¹ at 1 A g ⁻¹	6 M KOH	−0.2–0.7 V (SCE)			106
Co ₃ O ₄ @N-pc/PEDOT	305.3 F g ⁻¹ at 0.6 A g ⁻¹	1 M KOH	0–0.45 V (Ag/AgCl)		84% (3000)	107
CuCo ₂ O ₄ @40-rGO	762 F g ⁻¹ at 0.5 A g ⁻¹	6 M KOH	0–0.6 V (Ag/AgCl)	71.6% (0.5 to 20 A g ⁻¹)	108% (5000)	108
Pt-NiCo ₂ O ₄ /C	1665.3 F g ⁻¹ at 1 A g ⁻¹	6 M KOH	0–0.4 V (SCE)		94.49% (3500)	109
FeNiCo ZIF-67 (1 : 2 : 1)	532.7 F g ⁻¹ at 1 A g ⁻¹	3 M KOH	−0.3–0.25 V (Ag/AgCl)	41.4% (1 to 10 A g ⁻¹)	91% (10 000)	110
Co ₃ O ₄ -carbon	574.44 F g ⁻¹ at 1 A g ⁻¹	6 M KOH	0–0.5 V (Ag/AgCl)	52.6% (1 to 20 A g ⁻¹)	94.7% (1000)	111

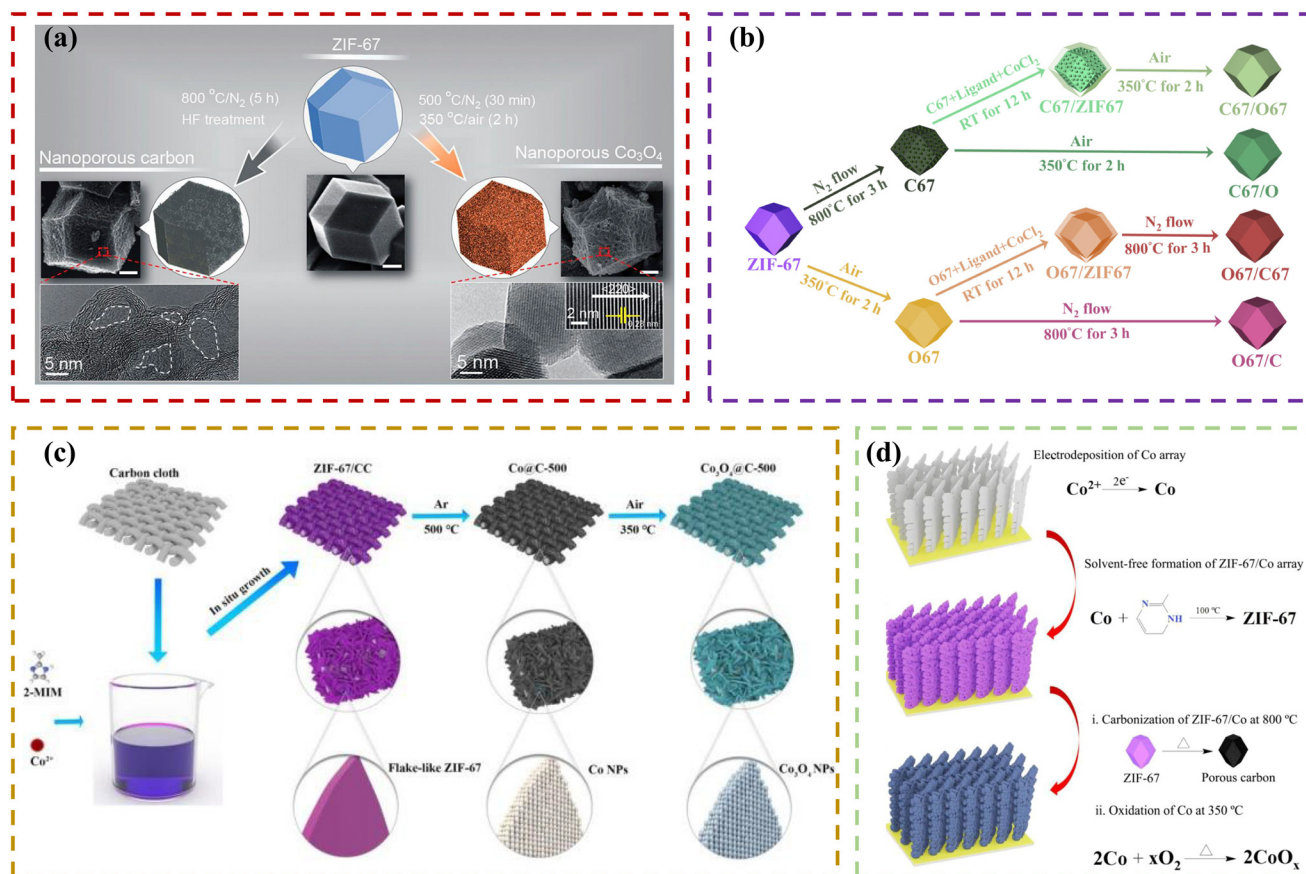


Fig. 2 (a) Schematic of the process for the preparation of nanoporous carbon and nanoporous Co_3O_4 from a ZIF-67 polyhedron as the single precursor by optimized thermal treatment. The actual SEM images and high-resolution TEM images of the respective materials are shown below their illustrations. Reprinted with permission from ref. 49, Copyright 2015, the American Chemical Society. (b) Illustration of the process for the synthesis of C67, C67/O67, C67/O, O67, O67/C67 and O67/C. Reprinted with permission from ref. 112, Copyright 2021, Elsevier Ltd. (c) Schematic of the formation of $\text{Co}_3\text{O}_4/\text{C}$ nanosheet array. Reprinted with permission from ref. 77, Copyright 2021, Elsevier B.V. (d) Schematic of the process for the preparation of $\text{CoO}_x/\text{carbon}$ arrays. Reprinted with permission from ref. 81, Copyright 2021, the American Chemical Society.

cycling process. To compare the influence of the order of the two-step calcination in the oxide/carbon composite materials, Chen *et al.*¹¹² synthesized six active materials including carbonized ZIF67 (C67), oxidized C67 (C67/O), oxidized ZIF67-covered C67 (C67/O67), oxidized ZIF67 (O67), carbonized O67 (O67/C) and carbonized ZIF67-covered O67 (O67/C67) (shown in Fig. 2b). Among them, the C67/O electrode showed the highest capacitance value of 332.3 mF cm^{-2} at 20 mV s^{-1} due to the suitable N-doped graphite and Co_3O_4 composition as well as the porous particle-assembled polyhedron structure. Similarly, as shown in Fig. 2c, Shu *et al.*⁷⁷ grew flake-like ZIF-67 on carbon cloth, and subsequently synthesized $\text{Co}_3\text{O}_4/\text{C}$ by adopting a similar two-step thermal conversion. As a result, this strategy effectively prevents structural collapse and defect formation, which are usually caused by the direct oxidation of ZIF-67 nanosheets. In supercapacitor tests, $\text{Co}_3\text{O}_4/\text{C}$ -500 showed an appreciable specific capacitance (703.3 F g^{-1} at 1 A g^{-1}) and excellent cycling stability with the capacitance retention of 100% after 10 000 cycles at 10 A g^{-1} . Moreover, the $\text{Co}_3\text{O}_4/\text{C}$ -500/reduced graphene oxide (RGO) asymmetric supercapacitor (ASC) exhibited an energy density

of $43.99 \text{ W h kg}^{-1}$ at a power density of 824.8 W kg^{-1} , and excellent cycling performance with a capacity retention of 88% after 10 000 cycles. This excellent performance was attributed to the rational composition control and unique structure of Co_3O_4 nanoparticles embedded in the carbon skeleton, which resulted in short electrolyte diffusion channels as well as electron transport distance and effectively reduced the negative effect of volume change in the electrode materials during the charge/discharge process. Alternatively, Li *et al.*⁸¹ prepared tree-like $\text{CoO}_x/\text{carbon}$ on Au surface *via* a chemical vapor deposition method and two-step treatment, as shown in Fig. 2d. The as-prepared $\text{CoO}_x/\text{carbon}$ composite arrays provided a less tortuous pathway for ion diffusion, high pseudocapacitance from the transition metal oxide, and good electrical conductivity from carbon. Moreover, the absence of adhesives in array electrodes is beneficial for the promotion of the electrochemical performance. Subsequently, Wang *et al.*⁹⁵ changed the order of the two-step thermal treatment method to obtain $\text{Co}_3\text{O}_4/\text{NC}$. $\text{Co}_3\text{O}_4/\text{NC}$ exhibited a specific capacitance of 1144 F g^{-1} at a current density of 1 A g^{-1} (much higher than the specific capacitance of pure Co_3O_4), and its retention rate was 45.4% at a

current density of 20 A g^{-1} . In addition, the asymmetric supercapacitor (ASC) device consisting of $\text{Co}_3\text{O}_4/\text{NC}$ composite electrodes and activated carbon produced the highest energy density of 40 W h kg^{-1} at a power density of 1037 W kg^{-1} . At a current density of 5 A g^{-1} , the capacitor retained 87.6% of its initial capacitance after 10 000 charge/discharge cycles.

2.2 Multi-metal oxides

The doping of other metal ions in the precursor ZIF-67 can be performed to derive more transition metal oxides. Also, multi-metal oxides can provide a higher theoretical capacitance because of the greater number of changes in their valence state. Chu *et al.*⁶⁹ designed a three-dimensional hollow CoWO_4 composite grown on Ni-foam ($3\text{D-H-CoWO}_4/\text{NF}$) based on a flower-like ZIF-67 utilizing a facile dipping and hydrothermal approach. $3\text{D-H-CoWO}_4/\text{NF}$ not only possessed a large specific area and rich active sites, but also accommodated the volume expansion/contraction during the charge/discharge processes. Additionally, its unique structure facilitated fast electron/ion transport, resulting in a high specific capacitance of 1395 F g^{-1} and an excellent cycle stability with 89% retention after 3000 cycles and superior rate property. Furthermore, $3\text{D-H-CoWO}_4/\text{NF}$ could be used as a cathode to assemble an asymmetric supercapacitor (ASC), and $3\text{D-H-CoWO}_4/\text{NF}/\text{AC}$ showed a good energy density (29.0 W h kg^{-1}). Similarly, Le *et al.*⁷⁰ designed $\text{Co}_2\text{V}_2\text{O}_7/\text{graphene}$ composites through an *in situ* ion exchange reaction, as shown in Fig. 3g. The morphological and compositional characterization confirmed that ZIF-67 was successfully transformed into the nanoparticle-assembled hollow $\text{Co}_2\text{V}_2\text{O}_7$ nanocages, which were densely distributed on graphene (shown in Fig. 3a–f). Benefiting from the well-

designed structure and compositions, the electrochemical tests indicated that the as-prepared $\text{Co}_2\text{V}_2\text{O}_7/\text{graphene}$ electrode exhibited a high specific capacity of 276.5 C g^{-1} at 1 A g^{-1} , good rate capability (Fig. 3h), and remarkably long cycling stability (93% capacity retention after 10 000 cycles). The asymmetric supercapacitor devices assembled with $\text{Co}_2\text{V}_2\text{O}_7/\text{graphene}$ and reduced graphene oxides delivered a high energy density of 25.7 W h kg^{-1} at a power density of 663.5 W kg^{-1} and excellent long cycling stability.

Moreover, the doping of metal ions in the process of forming the precursor ZIF-67 or *in situ* ion exchange reaction of the precursor ZIF-67 is also an important approach to obtain multi-metal oxides. Cheng *et al.*⁷² synthesized three-dimensional porous iron-doped Co_3O_4 using a single bi-metallic metal–organic framework, FeCo-ZIF-67 (Fig. 4a). The optimal 3D porous Fe-doped Co_3O_4 possessed a high capacitance of 767.9 C g^{-1} at 1 A g^{-1} . Also, the Fe-doped $\text{Co}_3\text{O}_4/\text{N-doped carbon HSC}$ device achieved a desirable specific energy (37 W h kg^{-1}) and power (750 W kg^{-1}), and satisfactory cycling stability (90% retention after 4000 cycles). Similarly, Venkatesh *et al.*⁹¹ reported the synthesis of NiCo_2O_4 nanosheets based on NiCo-MOFs and combined them with graphene oxide due to its outstanding mechanical support and electronic conductivity. The NiCo_2O_4 nanosheets/graphene nanosheets achieved a high specific capacitance of 1365 F g^{-1} at 1 A g^{-1} and excellent capacity retention of 89.11% over 2000 cycles at 10 A g^{-1} . As shown in Fig. 4b, Zheng *et al.*¹⁰⁶ used pure ZIF-67 as the precursor to fabricate $\text{CoFe}_2\text{O}_4\text{-Fe@NC}$ particles with a high surface area, which helped to accelerate ion and charge transfer. The specific capacitance of the $\text{CoFe}_2\text{O}_4\text{-Fe@NC}$ composite carbonized at 700°C reached

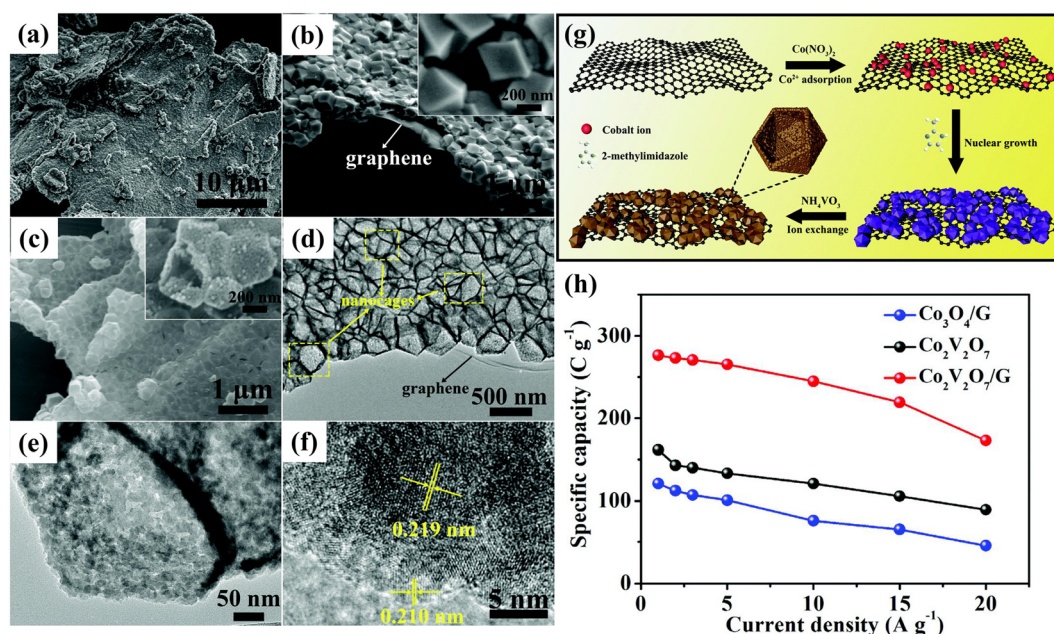


Fig. 3 (a and b) SEM images of ZIF-67/G; (c) SEM image, (d and e) TEM images, and (f) HR-TEM image of $\text{Co}_2\text{V}_2\text{O}_7/\text{G}$. (g) Schematic of the fabrication process for $\text{Co}_2\text{V}_2\text{O}_7/\text{G}$. (h) Specific capacitance of $\text{Co}_2\text{V}_2\text{O}_7$, $\text{Co}_2\text{V}_2\text{O}_7/\text{G}$ and $\text{Co}_3\text{O}_4/\text{G}$ electrodes at different current densities. Reprinted with permission from ref. 70, Copyright 2020, The Royal Society of Chemistry.

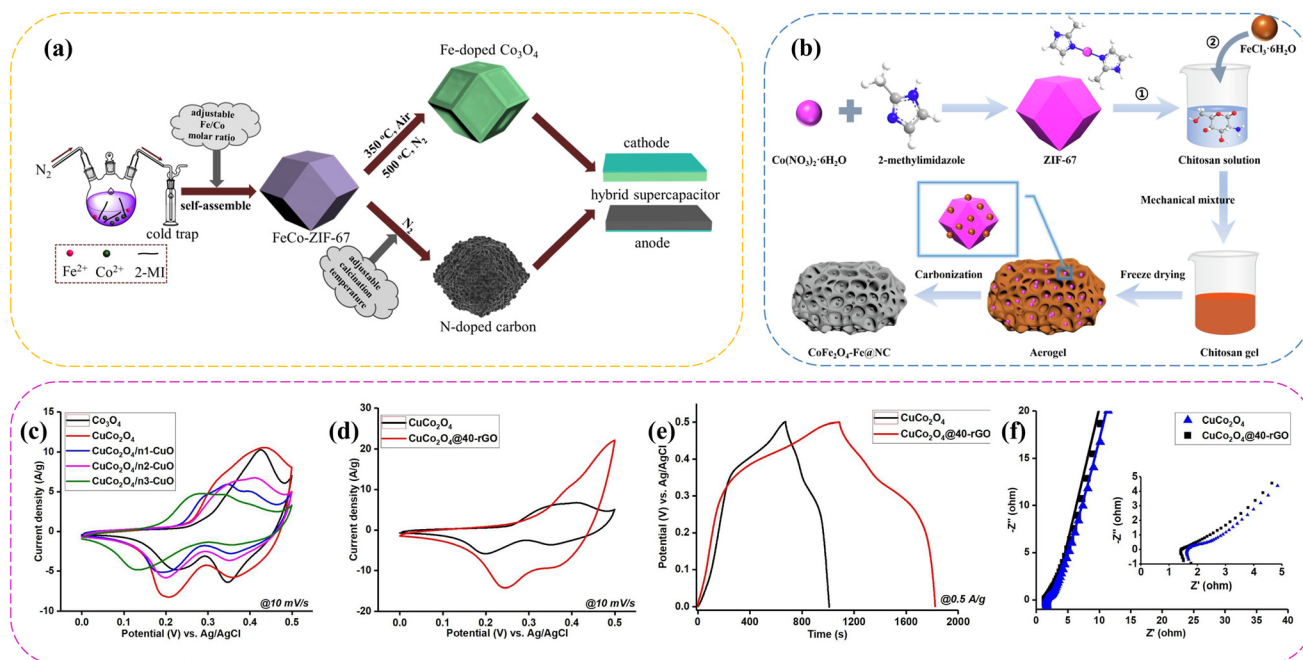


Fig. 4 (a) Schematic of the design of Fe-doped Co₃O₄ and N-doped carbon. Reprinted with permission from ref. 72, Copyright 2020, Elsevier Inc. (b) Procedure for the synthesis of the CoFe₂O₄-Fe@NC composite material. Reprinted with permission from ref. 106, Copyright 2024 Elsevier Inc. (c) CV curves of the metal oxide electrodes at a scan rate of 10 mV s⁻¹; (d) CV curves of CuCo₂O₄ and CuCo₂O₄@40-rGO at 10 mV s⁻¹; (e) GCD curves of CuCo₂O₄ and CuCo₂O₄@40-rGO at a current density of 0.5 A g⁻¹; and (f) Nyquist plots of CuCo₂O₄ and CuCo₂O₄@40-rGO. Reprinted with permission from ref. 108, Copyright 2024, Elsevier B.V.

3960.9 F g⁻¹ at 1 A g⁻¹. When this composite was combined with activated carbon (AC) to construct an asymmetric supercapacitor (ASC), a density of energy of up to 84.9 W h kg⁻¹ was attained at a power capacity of 291.6 W kg⁻¹. Moreover, this composite maintained a capacitance retention of up to 94.9% after 10 000 cycles. At the same time, Semerci *et al.*¹⁰⁸ prepared CuCo₂O₄@rGO nanomaterials using a step-wise method, which involved the annealing of the CoCu-LDH@rGO precursor derived from ZIF-67@rGO. At a graphene concentration of 4.1%, the composite named CuCo₂O₄@40-rGO exhibited the best performance among the CuCo₂O₄@rGO composites (Fig. 4c-f). A specific capacity of 762 F g⁻¹ (381 C g⁻¹) was recorded at a current density of 0.5 A g⁻¹ and an excellent rate performance of 71.6%, revealing an excellent capacitive performance and reversibility. Moreover, the electrochemical performance of CuCo₂O₄@40-rGO was evaluated as a cathodic electrode and biomass-derived activated carbon (AC) as the negative electrode. The hybrid supercapacitor device showed an energy density of 20.7 W h kg⁻¹ at a power density of 0.43 kW kg⁻¹ with a working potential window of 0–1.7 V, as well as 98.8% capacity retention over 10 000 cycles. Also, Wei *et al.*⁵⁴ reported the synthesis of hybrid porous Co₃O₄-CeO₂ hollow polyhedrons *via* a simple cation-exchange route, followed by heat treatment. When utilized as the electrode material for supercapacitors, the hybrid porous Co₃O₄-CeO₂ hollow polyhedrons delivered a large specific capacitance of 1288.3 F g⁻¹ at 2.5 A g⁻¹ and a remarkably long cycling stability (<3.3% loss after 6000 cycles). Furthermore, an asymmetric

supercapacitor (ASC) device based on the hybrid porous Co₃O₄-CeO₂ hollow polyhedrons was assembled. The ASC device possessed an energy density of 54.9 W h kg⁻¹, which retained 44.2 W h kg⁻¹ even at a power density of 5100 W kg⁻¹, indicating its promising application in electrochemical energy storage.

2.3 Composite materials

It is estimated that particle-shaped metal oxides usually experience high internal resistance, and consequently reduced charge transfer due to the agglomeration of the particles. In this regard, ZIF-67-derived oxides are usually composited with other materials to improve their electrochemical properties, such as carbon materials and conductive polymers to improve their conductivity or other transition metal compounds to achieve a higher specific capacitance.

Deng *et al.*⁵² successfully prepared honeycomb-like porous Co₃O₄ grown on three-dimensional graphene network/nickel foam (Co₃O₄/3DGN/NF) *via* a facile solution growth process with subsequent annealing treatment, as shown in Fig. 5a. Fig. 5b shows Co₃O₄/3DGN grown on Ni foam, which possessed a large specific surface area, as shown in Fig. 5c. Also, the Co₃O₄/3DGN/NF electrode delivered a high specific capacitance (321 F g⁻¹ at 1 A g⁻¹) and excellent long-cycling stability (88% of its maximum capacitance after 2000 charge-discharge cycles). Furthermore, the Co₃O₄/3DGN/NF electrode exhibited the maximum energy density of 7.5 W h kg⁻¹ with the power density of 794 W kg⁻¹ and retained 4.1 W h kg⁻¹ at the power

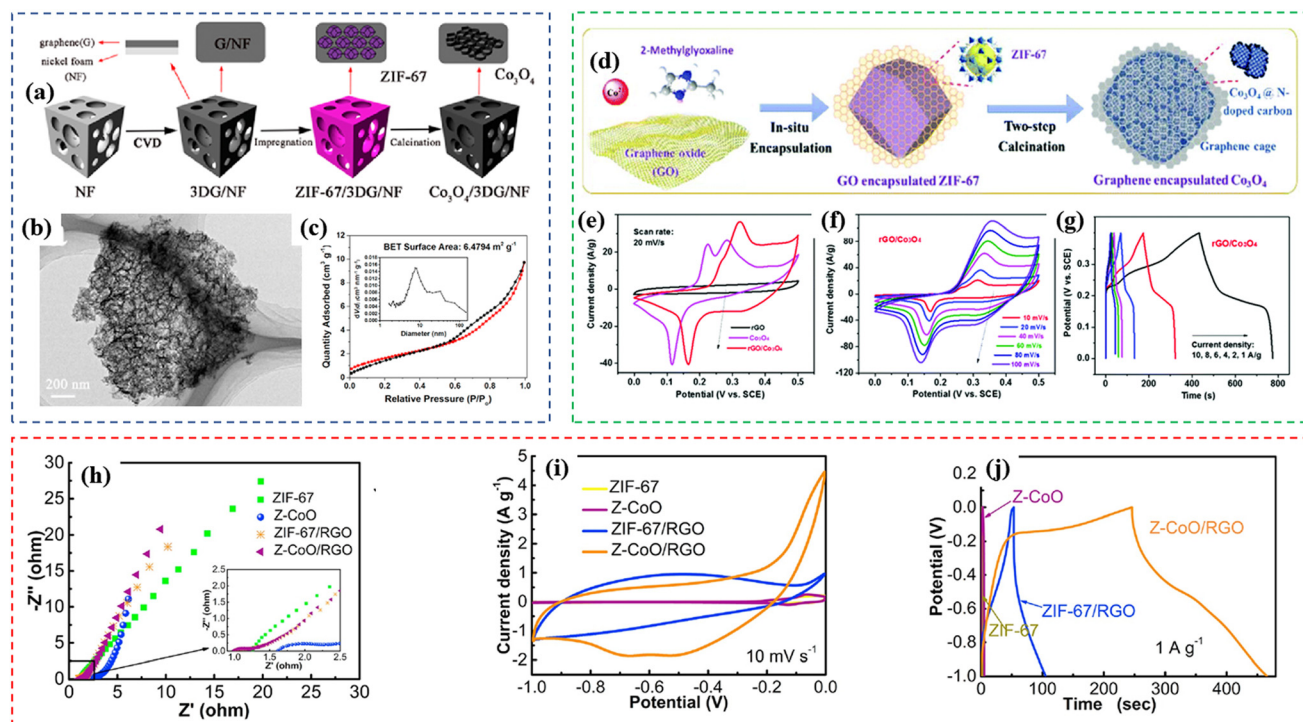


Fig. 5 (a) Schematic of the fabrication process for Co₃O₄/3DGN/NF; (b) TEM image of Co₃O₄/3DGN/NF; and (c) pore size distribution of Co₃O₄/3DGN/NF. Reprinted with permission from ref. 52, Copyright 2016, Elsevier B.V. (d) Schematic of the synthesis route for rGO/Co₃O₄ composite; (e) CV curves of rGO, Co₃O₄, and rGO/Co₃O₄ at 20 mV s⁻¹; (f) CV curves of rGO/Co₃O₄ at different scan rates; and (g) GCD curves of rGO/Co₃O₄ at different current densities. Reprinted with permission from ref. 60, Copyright 2019, The Royal Society of Chemistry. (h) Nyquist impedance plots, (i) CV curves and (j) GCD curves of ZIF-67, Z-CoO, ZIF-67/RGO and Z-CoO/RGO. Reprinted with permission from ref. 71, Copyright 2020, Elsevier Ltd.

density of 15 kW kg⁻¹ in a two-electrode system. Its enhanced electrochemical properties can be attributed to the unique nanostructure of Co₃O₄ with admirable pseudocapacitance performance and the intimate integration of graphene with Co₃O₄ and the Ni foam matrix, which not only enhanced the electron conductivity for fast electron and ion transport but also provided a high specific surface area and excellent structural stability. Similarly, Lin *et al.*⁶⁰ obtained rGO/Co₃O₄ via the *in situ* growth of ZIF-67 polyhedra in the presence of graphene oxide, followed by thermal annealing (Fig. 5d). The resultant rGO/Co₃O₄ composites consisted of a continuously-conductive double-network constructed from graphene sheets and derived N-doped carbons from ZIF-67, showing a large specific surface area of 523 m² g⁻¹. The as-fabricated symmetrical supercapacitor based on rGO/Co₃O₄ exhibited a high specific capacitance of 277.5 F g⁻¹ at 25 A g⁻¹ (as compared in Fig. 5e–g) and an energy density of 24.7 W h kg⁻¹ at a power density of up to 40 kW kg⁻¹. The supercapacitor also retained 87.5% of its initial capacitance over 5000 cycles at 5 A g⁻¹. The large capacitance, high energy density, and excellent cycling stability for rGO/Co₃O₄ can be attributed to the 3D double conductive network from the 2D graphene sheets and porous channels of the pseudo-capacitive Co₃O₄ polyhedra. Moreover, Zha *et al.*⁷¹ initially synthesized ZIF-67-derived CoO, and then formed a composite with reduced graphene oxide through the hydrothermal method. As shown in Fig. 5h–j, Z-CoO/RGO

exhibited an outstanding mass specific capacitance (275 F g⁻¹ at 1 A g⁻¹) and excellent resistance characteristic due to the synergistic effect between ZIF-67 and RGO. Besides graphene, Yang *et al.*⁹⁸ reported the preparation of ZIF-67-derived cobalt oxide/carbon nanotube (MWCNT_x@Co₃O₄) composites by calcining the MWCNT_x@ZIF-67 precursor in one step. Benefiting from the homogeneous conductive carbon nanotubes, the synthesized MWCNT_x@Co₃O₄ electrode displayed a maximum specific capacitance of 206.89 F g⁻¹ at 1 A g⁻¹.

Also, Chen's group⁹⁷ reported the synthesis and characterization of nanocomposites via a two-step method using polypyrrole (PPy) and Co₃O₄@SiO₂ in the presence of an oxidizing agent. As shown in Fig. 6a, Co₃O₄@SiO₂/PPy was obtained by coating PPy on Co₃O₄@SiO₂, which was prepared by annealing SiO₂-coated ZIF-67 at high temperature. Comparing Fig. 6b with Fig. 6c and d, it can be seen that PPy was well combined with Co₃O₄@SiO₂. Also, the results showed that the specific capacitance of Co₃O₄@SiO₂ and Co₃O₄@SiO₂/PPy (2 mL) was 33.36 F g⁻¹ and 107.7 F g⁻¹ at 0.6 A g⁻¹, indicating that the addition of PPy greatly improved the electrochemical performance of Co₃O₄@SiO₂ (as shown in Fig. 6e and f). This may be due to synergy between Co₃O₄@SiO₂ and the PPy polymer, where the addition of PPy may help construct more ion channels in Co₃O₄@SiO₂ to enhance the ion transport. Subsequently, the next year, Chen's group¹⁰⁷ again reported the preparation of the Co₃O₄@N-pc/PEDOT composite as an

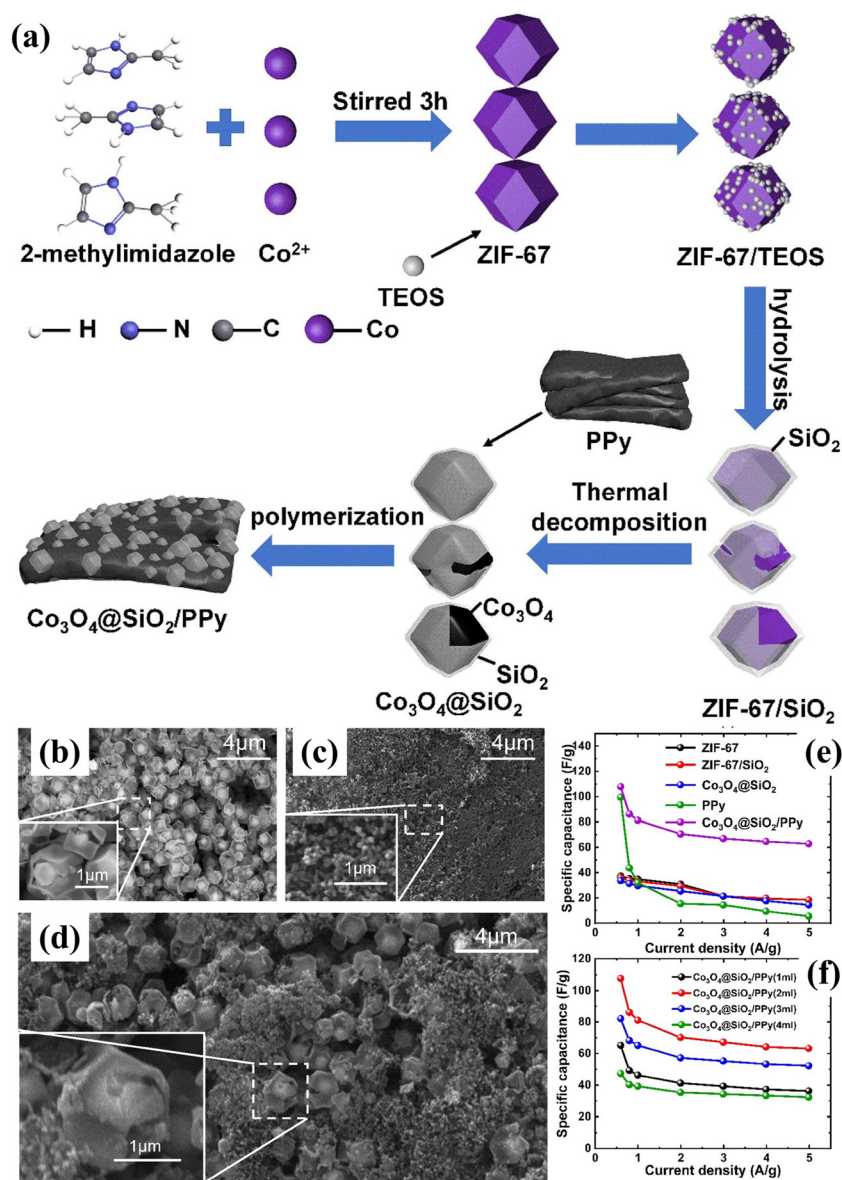


Fig. 6 (a) Schematic illustration of synthetic procedure for ZIF-67, ZIF-67/SiO₂, Co₃O₄@SiO₂ and Co₃O₄@SiO₂/PPy; SEM images of (b) Co₃O₄@SiO₂, (c) PPy and (d) Co₃O₄@SiO₂/PPy (2 mL); (e) specific capacitance as a function of current density for ZIF-67, ZIF-67/SiO₂, Co₃O₄@SiO₂, PPy and Co₃O₄@SiO₂/PPy; and (f) specific capacitance as a function of the current density for Co₃O₄@SiO₂ and PPy in different proportions. Reprinted with permission from ref. 97, Copyright 2023, Springer Nature.

electrode material for supercapacitors. Employing ZIF-67@ZIF-8 as the precursor, the obtained Co₃O₄@N-pc/PEDOT composite exhibited the highest specific capacitance of 305.3 F g⁻¹ at 0.6 A g⁻¹, which is significantly superior to that of PEDOT (63.6 F g⁻¹), ZIF-67@ZIF-8-400 (91.4 F g⁻¹), ZIF-67 (43.8 F g⁻¹) and Co₃O₄@N-pc-400 (154.8 F g⁻¹). Further, Co₃O₄@N-pc/PEDOT (4 mL) was used to construct a symmetric supercapacitor, which delivered outstanding values of energy (20.03 W h kg⁻¹) and power density (415.17 W kg⁻¹).

Wang *et al.*⁵³ used ZIF-67 and (NH₄)₂MoS₄ as the precursors of Co₃O₄/C and MoS₂, respectively, to obtain hierarchical mesoporous Co₃O₄/C@MoS₂ core-shell structure materials *via* calcination and solvothermal methods. Co₃O₄/C@MoS₂ exhibi-

ted a high specific capacitance (1076 F g⁻¹ at 1 A g⁻¹), rate capability (76.9% capacitance retention at 10 A g⁻¹) and cyclic stability (64.5% capacitance retention after 5000 cycles at 10 A g⁻¹) due to the presence of MoS₂, greatly influencing the electrochemical performances of the obtained core-shell materials, which were better than that of Co₃O₄/C. Xu *et al.*⁶⁷ reported the synthesis of a hollow Co₃O₄@MnO₂ cubic nano-material derived from the ZIF-67@Mn-ZIF sacrificial precursor. It demonstrated high performances, such as specific capacitance of 413 F g⁻¹ at the current density of 0.5 A g⁻¹, and when the current density increased from 0.5 to 10 A g⁻¹ (20 times increase), it still exhibited ~41% retention of its initial capacitance. Similarly, Babu *et al.*⁹³ also synthesized a type of

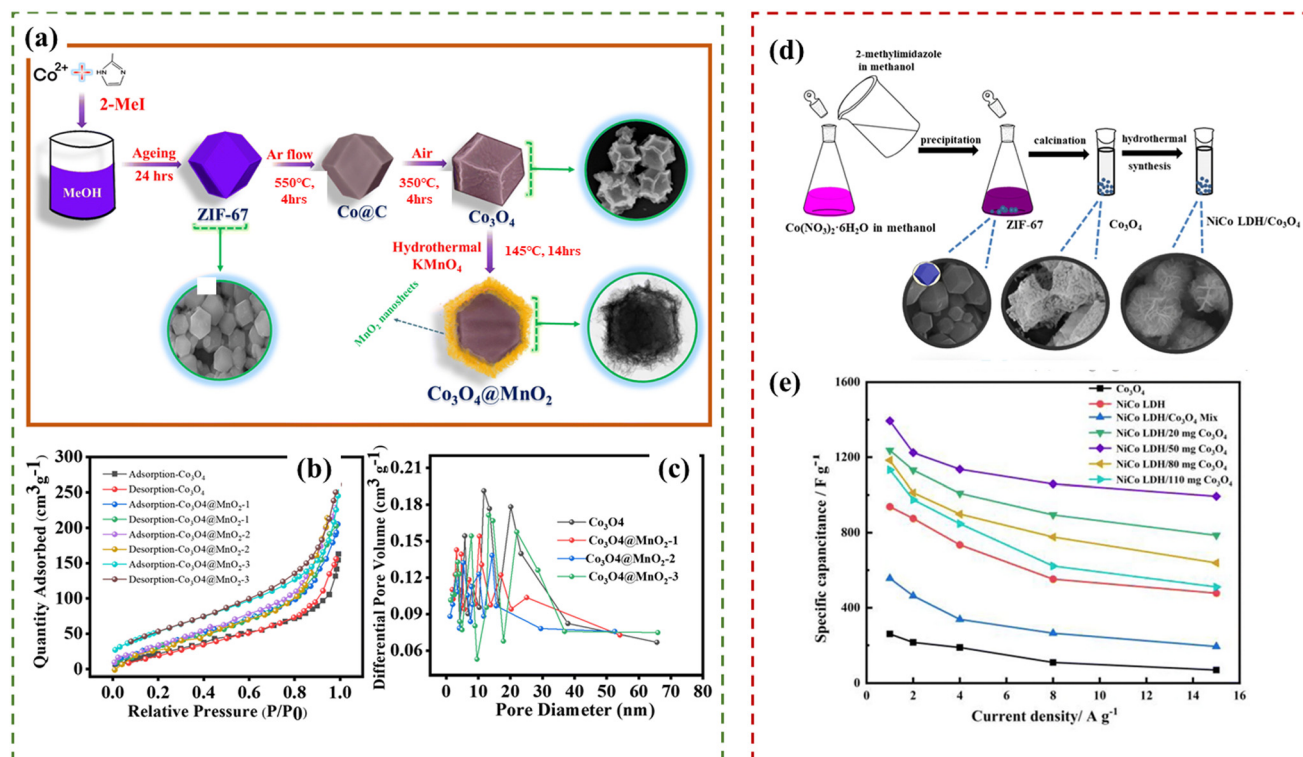


Fig. 7 (a) Schematic diagram of the synthesis of $\text{Co}_3\text{O}_4@/\text{MnO}_2$ core-shell structure; (b) BET analysis and (c) BJH pore size distribution curves of ZIF-67-derived Co_3O_4 , $\text{Co}_3\text{O}_4@/\text{MnO}_2$ -1, $\text{Co}_3\text{O}_4@/\text{MnO}_2$ -2 and $\text{Co}_3\text{O}_4@/\text{MnO}_2$ -3. Reprinted with permission from ref. 93, Copyright 2022, The Royal Society of Chemistry. (d) Schematic of the processes for the preparation of $\text{NiCo LDH}/\text{Co}_3\text{O}_4$; and (e) comparison of the specific capacitance of Co_3O_4 , NiCo LDH , $\text{NiCo LDH}/\text{Co}_3\text{O}_4$ Mix, $\text{NiCo LDH}/20 \text{ mg Co}_3\text{O}_4$, $\text{NiCo LDH}/50 \text{ mg Co}_3\text{O}_4$, $\text{NiCo LDH}/80 \text{ mg Co}_3\text{O}_4$ and $\text{NiCo LDH}/110 \text{ mg Co}_3\text{O}_4$ at different current densities. Reprinted with permission from ref. 65, Copyright 2019, Springer Nature.

$\text{Co}_3\text{O}_4@/\text{MnO}_2$ nanosheets using ZIF-67 and provided an effective pathway for rapidly transporting electrons and ions, as shown in Fig. 7a. As a result, the ZIF-67-derived $\text{Co}_3\text{O}_4@/\text{MnO}_2$ -3 electrode material showed a high specific capacitance of 768 C g^{-1} at 1 A g^{-1} with outstanding cycling stability (86% retention after 5000 cycles) and the porous structure of the material had a good BET surface area of $160.8 \text{ m}^2 \text{ g}^{-1}$ according to Fig. 7b and c. As a hybrid supercapacitor, $\text{Co}_3\text{O}_4@/\text{MnO}_2$ -3/activated carbon exhibited a high specific capacitance (82.9 C g^{-1}) and long cycle life (85.5% retention after 5000 cycles). Moreover, a high energy density of $60.17 \text{ W h kg}^{-1}$ and power density of $2674.37 \text{ W kg}^{-1}$ were achieved. Additionally, as shown in Fig. 7d, Dai *et al.*⁶⁵ modified ZIF-67-derived Co_3O_4 with NiCo -layered double hydroxide nanosheets to obtain an outstanding electrode composite material. The specific capacitance of $\text{NiCo LDH}/50 \text{ mg Co}_3\text{O}_4$ was 1393.9 F g^{-1} at 1 A g^{-1} with outstanding cycle stability (88.4% up to 5000 cycles) compared with other electrodes, as shown in Fig. 7e. An aqueous asymmetric supercapacitor (ASC) was assembled by employing $\text{NiCo LDH}/50 \text{ mg Co}_3\text{O}_4$ as the positive electrode and activated carbon (AC) as the negative electrode, which delivered a voltage window of 1.5 V and a high energy density of 46.4 W h kg^{-1} at a power density of 750.4 W kg^{-1} .

Considering two-electrode systems, El-Deen's group⁸⁹ further applied $\text{Ni-Co LDH}/\text{Co}_3\text{O}_4$ nanocubes (prepared as shown in

Fig. 8a) in an asymmetric solid-state supercapacitor device (ASC) and constructed the device based on a full cell with the $\text{Ni-Co LDH}/\text{Co}_3\text{O}_4$ nanocubes and three-dimensional spongy graphene. When tested in a two-electrode system, as shown in Fig. 8b–e, the ASC delivered the highest energy density of 66.7 W h kg^{-1} with a power density of 800 W kg^{-1} and superior recyclability over 10 500 cycles with a holding capacitance retention ratio of 90.5% and coulombic efficiency of 99.8%. Recently, Wang *et al.*⁹⁹ reported the preparation of hollow carbon tube@ $\text{Co}_3\text{O}_4@/\text{SnS}_2$ composites by growing ZIF-67 and SnS_2 nanosheets on a PMMA/PAN/ Zn^{2+} electrospun film as the precursors (Fig. 8f). The unique inner core-shell and the outer-shell SnS_2 contributed to the excellent characteristics, including abundant pores and channels for rapid ion transport and storage, high specific surface area, improved electrical conductivity, and additional electroactive sites for the faradaic reaction. Owing to the synergy between the unique 1D porous hollow structure and the different components, the as-fabricated HCT-2@ $\text{Co}_3\text{O}_4@/\text{SnS}_2$ electrode exhibited a high specific capacitance of 439 F g^{-1} at 1 A g^{-1} . Moreover, as shown in Fig. 8g, the assembled flexible supercapacitor also demonstrated a remarkable energy density of $40.22 \text{ W h kg}^{-1}$, the corresponding power density of 750.22 W kg^{-1} , and long cycle life (Fig. 8j). In addition, no structural deformation and capacitance loss were observed in the bent devices, as shown in Fig. 8h and i.

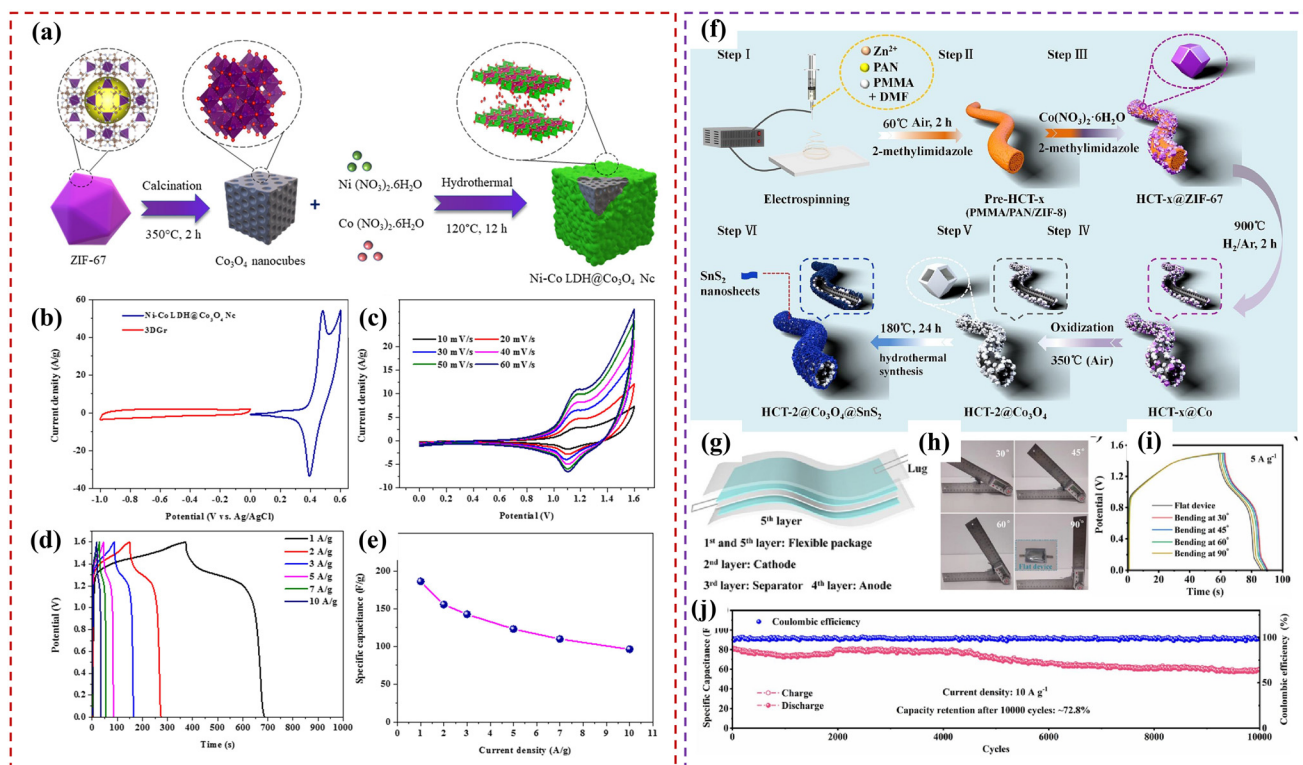


Fig. 8 (a) Schematic process for the fabrication of Ni-Co LDH@Co₃O₄ nanocube; (b) CV profiles of 3DSGr and Ni-Co LDH@Co₃O₄ nanocube electrodes at a scan rate of 10 mV s⁻¹; (c) CV plots of the ASC at various scan rates; (d) GCD curves of Ni-Co LDH@Co₃O₄ nanocube//3DSGr device at various current densities; and (e) capacitance measured for the prepared ASC device. Reprinted with permission from ref. 89, Copyright 2022, Elsevier B.V. (f) Schematic illustration of the preparation of HCT-2@Co₃O₄@SnS₂; (g) schematic illustration of HCT-2@Co₃O₄@SnS₂//AC device; (h) flexible device bending at various angles; (i) GCD plots of the ASC device at various bending conditions; and (j) cycling stability of the device at 10 A g⁻¹. Reprinted with permission from ref. 99, Copyright 2023, Elsevier B.V.

3. ZIF-67-derived transition metal sulfides

As a type of pseudocapacitor material, sulfides possess larger specific capacitance values, narrower band gaps, lower melting points, higher conductivity and richer redox sites compared to metal oxides. However, they still have some challenges, which limit their further research such as side reactions during the electrochemical measurement process, susceptibility to oxidation and structural destruction.³⁴ Thus, to solve the above-mentioned problems, the design of the material structure needs to be studied, while ZIF-67 is regarded as a good precursor to obtain transition metal sulfides with unique structures¹¹³ (Table 2).

3.1 Single metal sulfides

Hu *et al.*¹¹⁴ demonstrated the template-induced formation of double-shelled hollow structures with CoS-nanoparticle-assembled nanoboxes surrounded by outer CoS-nanosheet-constructed shells (CoS-NP/CoS-NS DSNBs). Delicate manipulation of the template-induced reaction between ZIF-67 and water led to the formation of ZIF-67/Co(OH)₂-nanosheet yolk-shelled structures, which were then transformed into CoS-NP/

CoS-NS DSNBs through the reaction with Na₂S, as shown in Fig. 9a. As a result of the unique assembly of subunits with different dimensionalities, the CoS-NP/CoS-NS DSNBs possessed a high specific surface area, suitable mesopores, and good structural robustness (Fig. 9b and c), which contributed to their exceptional performance as a battery-type electrode (a specific capacitance of 980 F g⁻¹ at 1 A g⁻¹ and 89% retention after 10 000 cycles in Fig. 9d). Additionally, as shown in Fig. 9e, Jia *et al.*¹²¹ reported the designed synthesis of porous quadruple-shelled CoS₂ hollow dodecahedrons with concave surfaces through a template-induced formation process. As the result of the combined advantages of the materials and structures (Fig. 9f), when evaluating as electrodes for supercapacitors, the porous quadruple-shelled CoS₂ showed a high specific capacity of 375.2 C g⁻¹ with a good rate performance and excellent stability with 92.1% retention after 10 000 cycles. Moreover, the assembled quadruple-shelled CoS₂//active carbon asymmetric supercapacitor achieved a high energy density of 52.1 W h kg⁻¹, excellent specific capacitance (146 F g⁻¹ at 0.5 A g⁻¹), and electrochemical cycling stability (89% retention after 5000 cycles). Moreover, Peng *et al.*¹³⁶ successfully synthesized hierarchical porous Co₉S₈ nanowire arrays grown on Ni foam *via* a multi-step method for use in supercapacitors (Fig. 9g). Introducing ZIF-67 is favorable for the for-

Table 2 Summary of the electrochemical characteristics of ZIF-67-derived sulfide materials in three-electrode measurements

Electrode materials	Specific capacity	Electrolyte	Potential window (CV)	Capacity retention	Cyclic stability	Ref.
CoS-NP/CoS-NS	980 F g ⁻¹ at 1 A g ⁻¹	2 M KOH	0–0.6 V (SCE)	60% (1–20 A g ⁻¹)	89% (10 000)	114
CoNi ₂ S ₄	1890 F g ⁻¹ at 4 A g ⁻¹	2 M KOH	0–0.5 V (Ag/AgCl)	81.2% (4–20 A g ⁻¹)	71.6% (5000)	32
Co ₉ S ₈ @N–C@MoS ₂	410 F g ⁻¹ at 10 A g ⁻¹	3 M KOH	0–0.6 V (Hg/HgO)	79.8% (0.5–20 A g ⁻¹)	101.7% (20 000)	115
NiCo ₂ S ₄	939 C g ⁻¹ at 1 A g ⁻¹	6 M KOH	–0.1–0.6 V (SCE)	75.8% (1–10 A g ⁻¹)		116
CNT/CoS	2173.1 F g ⁻¹ at 5 A g ⁻¹	6 M KOH	–0.07–0.63 (Hg/HgO)	65% (5–20 A g ⁻¹)		117
GH@NC@Co ₉ S ₈	842.4 F cm ⁻² at 1 A g ⁻¹	6 M KOH	0–0.5 V (Ag/AgCl)	65.5% (1–10 A g ⁻¹)		118
MnO ₂ @NiCo-LDH/CoS ₂	1547 F g ⁻¹ at 1 A g ⁻¹	2 M KOH	0–0.55 V (SCE)	76.9% (1–10 A g ⁻¹)	82.3% (2000)	119
NiCo ₂ S ₄	1232 F g ⁻¹ at 2.1 A g ⁻¹	3 M KOH	0–0.65 V (Hg/HgO)	55% (2.1–41.5 A g ⁻¹)	80% (8000)	120
CoS ₂	375.2 C g ⁻¹ at 1 A g ⁻¹	2 M KOH	–0.2–0.6 V (Hg/HgO)	70% (1–20 A g ⁻¹)	92.1% (10 000)	121
Mo-doped CoS HNC	781 F g ⁻¹ at 0.5 A g ⁻¹	2 M KOH	0–0.6 V (SCE)	52% (0.5–10 A g ⁻¹)	46.8% (5000)	122
CoS _x /Ni–Co LDH	1562 F g ⁻¹ at 1 A g ⁻¹	2 M KOH	–0.1–0.55 V (SCE)	65.4% (1–20 A g ⁻¹)	76.64% (5000)	123
CoS _x @NiCo-LDH	680.8 C g ⁻¹ at 1 A g ⁻¹	3 M KOH	0–0.6 V (Ag/AgCl)	76% (1–10 A g ⁻¹)	80% (3000)	124
NiCo ₂ S ₄	1382 F g ⁻¹ at 1 A g ⁻¹	2 M KOH	0–0.5 V (Ag/AgCl)	83.6% (1–10 A g ⁻¹)	70% (10 000)	125
CuCo ₂ S ₄	1344 F g ⁻¹ at 1 A g ⁻¹	3 M KOH	0–0.6 V (Hg/HgO)	71.3% (1–30 A g ⁻¹)	93.1% (5000)	126
Co ₃ S ₄ -HNCs@PPy	1706 F g ⁻¹ at 1 A g ⁻¹	2 M KOH	–0.1–0.8 V (SCE)	73.2% (1–10 A g ⁻¹)	68.1% (5000)	37
Co ₃ S ₄ @NiO	187.93 F g ⁻¹ at 1 A g ⁻¹	6 M KOH	0–0.5 V (SCE)	74.1% (1–20 A g ⁻¹)	92.6% (10 000)	127
MnCo ₂ S ₄ /Co ₉ S ₈	1058 F g ⁻¹ at 1 A g ⁻¹	6 M KOH	0–0.5 V (Hg/HgO)	47.6% (1–10 A g ⁻¹)		128
Co ₃ S ₄ /WS ₂	412.7 F g ⁻¹ at 1 A g ⁻¹	1 M H ₂ SO ₄	0–1 V (Ag/AgCl)		94.3% (2000)	129
NiCo ₂ S ₄	1350 F g ⁻¹ at 1 A g ⁻¹	2 M KOH	0–0.6 V (Hg/HgO)	70% (1–20 A g ⁻¹)		130
Co–W–S@N, S-PC	1001 F g ⁻¹ at 2 A g ⁻¹	2 M KOH	0–0.5 V (SCE)	45% (2–20 A g ⁻¹)		131
Co ₃ S ₄ /PANI	1106 F g ⁻¹ at 1 A g ⁻¹	6 M KOH	0–0.5 V (SCE)	66.55% (1–10 A g ⁻¹)	86% (20 000)	132
rGO/CoS _x -rGO/rGO	460 F g ⁻¹ at 1 A g ⁻¹	1 M KOH	0–0.5 V (SCE)	30% (1–16 A g ⁻¹)	85% (5000)	133
NiCoS@PPy	2316.6 F g ⁻¹ at 1 A g ⁻¹	2 M KOH	0–0.6 V (SCE)	60.8% (1–10 A g ⁻¹)		134
α-MnS@Co ₃ S ₄	283.3 mA h g ⁻¹ at 1 A g ⁻¹	6 M KOH	0–0.5 V (Ag/AgCl)	81.5% (1–25 A g ⁻¹)	92.7% (10 000)	135
Co ₉ S ₈ /NF	369.1 mA h g ⁻¹ at 1 A g ⁻¹	6 M KOH	0–0.5 V (Hg/HgO)	75.5% (1–20 A g ⁻¹)	75% (5000)	136
CoNi ₂ S ₄ /MXene/NF	933 C g ⁻¹ at 1 A g ⁻¹	3 M KOH	0–0.7 V (Hg/HgO)	70.2% (1–10 A g ⁻¹)		137
NiCo-LDH/Co ₉ S ₈	1654 F g ⁻¹ at 2 A g ⁻¹	3 M KOH	0–0.5 V (SCE)	83.3% (2–20 A g ⁻¹)	82.5% (5000)	138
CoNi ₂ S ₄	2448 F g ⁻¹ at 1 A g ⁻¹	3 M KOH	0–0.43 C	63.3% (1–10 A g ⁻¹)		139
hollow tube@sheets NiCo ₂ S ₄	3227.94 F g ⁻¹ at 2 A g ⁻¹	2 M KOH	0–0.7 V (SCE)	59% (2–10 A g ⁻¹)	83.92% (5000)	140
Al-doped Co ₉ S ₈ @NG	736 C g ⁻¹ at 1 A g ⁻¹	2 M KOH	–0.2–0.6 V (Ag/AgCl)	71% (1–40 A g ⁻¹)	92% (10 000)	141
MSZ@NF	4840 mF cm ⁻² at 1 mA cm ⁻²	2 M KOH	0–0.6 V		81.3% (5000)	142
Co _{1-x} S/HNPSCS	1058.9 C g ⁻¹ at 1 A g ⁻¹	6 M KOH	0–0.6 V (SCE)	74.3% (1–20 A g ⁻¹)		143
Co ₃ S ₄ /Ti ₃ C ₂ T _x	602 F g ⁻¹ at 1 A g ⁻¹	3 M KOH	0–0.6 V (Hg/HgO)	81.6% (1–10 A g ⁻¹)		144
CC/Co ₉ S ₈ /PPy	429 F g ⁻¹ at 1 mA cm ⁻²	2 M KOH	–0.2–0.6 V (SCE)	66.6% (1–16 mA cm ⁻²)	83.5% (2500)	145
rGO@CuCo ₂ S ₄ @CoS ₂ /NF	2447.1 F g ⁻¹ at 1 A g ⁻¹	6 M KOH	0–0.5 V (Hg/HgO)	55.2% (1–10 A g ⁻¹)	79.2% (10 000)	146
CoS/NC	789 F g ⁻¹ at 1 A g ⁻¹	6 M KOH	0–0.5 V (Hg/HgO)	80.2% (1–20 A g ⁻¹)	92.8% (10 000)	147
MoS ₂ @CoS ₂	950 F g ⁻¹ at 1 A g ⁻¹	2 M KOH	–0.2–0.8 V (SCE)	75.6% (1–10 A g ⁻¹)	94.6% (10 000)	148
N-Co ₃ S ₄ -GN/CNT	1158 F g ⁻¹ at 1 A g ⁻¹	6 M KOH	0–0.6 V (Hg/HgO)	86% (1–10 A g ⁻¹)	97.2% (4000)	149
Co-NTC@Co ₃ S ₄	3117.3 F g ⁻¹ at 1 A g ⁻¹	1 M KOH	0–0.45 V (SCE)	80% (1–10 A g ⁻¹)	87% (1000)	150
NiS ₂ /CoS ₂ @C	1373 C g ⁻¹ at 1 A g ⁻¹	6 M KOH	0–0.7 V (SCE)	68.6% (1–20 A g ⁻¹)	100.2% (10 000)	151
V ₂ O ₅ @Co ₃ S ₄	1493.6 F g ⁻¹ at 1 A g ⁻¹	2 M KOH	0–0.5 V (SCE)	57.9% (1–20 A g ⁻¹)	75.1% (7000)	152
CoNi ₂ S ₄ /MXene	751 C g ⁻¹ at 1 A g ⁻¹	3 M KOH	0–0.7 V	73.2% (1–10 A g ⁻¹)	72.1% (5000)	153
Co ₃ S ₄ @CoCH/NF	2697.1 F g ⁻¹ at 2 A g ⁻¹	3 M KOH	–0.05–0.55 V (SCE)	84.4% (2–20 A g ⁻¹)	79.8% (8000)	154
NiCo ₂ S ₄ /Co ₃ S ₄	8.43 F cm ⁻² at 2 mA cm ⁻²	3 M KOH	0–0.7 V (SCE)	24.9% (2–50 mA cm ⁻²)	60% (5000)	155
Co ₄ S ₃ /Ni ₃ S ₂ @MoS ₂	1238 F g ⁻¹ at 1 A g ⁻¹	1 M KOH	–0.1–0.8 V (Ag/AgCl)	56.9% (1–8 A g ⁻¹)	85% (2000)	156
NF/FeNi ₂ S ₄ @Co ₉ S ₈ -rGO	1308 C g ⁻¹ at 1 A g ⁻¹	6 M KOH	0–0.7 V (Ag/AgCl)	83.6% (1–36 A g ⁻¹)	93.75 (8500)	157
CoS ₂ @C	1151 F g ⁻¹ at 1 A g ⁻¹	2 M KOH	0–0.6 V (SCE)	73.4% (1–10 A g ⁻¹)	85.58% (10 000)	158
Ni(OH) ₂ /CoS/CC	561.6 mA h g ⁻¹ at 1 A g ⁻¹	2 M KOH	0–0.8 V (Hg/HgO)	70.8% (1–32 A g ⁻¹)		159
NiCo ₂ S ₄	408 mA h g ⁻¹ at 1 A g ⁻¹	6 M KOH	0–0.6 V (Hg/HgO)	51.1% (1–20 A g ⁻¹)	84.3% (10 000)	160
rGO/NiCo ₂ S ₄	171 mA h g ⁻¹ at 1 A g ⁻¹	2 M KOH	0–0.7 V (Hg/HgO)	71.3% (1–10 A g ⁻¹)	85% (2000)	161
CoS ₂ @gC/rGO	1188 F g ⁻¹ at 1 A g ⁻¹	1 M KOH	0–0.4 V (Ag/AgCl)	57% (1–20 A g ⁻¹)	76% (10 000)	162
CoS _x @CoNi ₂ S ₄ /CC	1970 F g ⁻¹ at 1 A g ⁻¹	1 M KOH	0–0.6 V (Hg/HgO)	92% (1–10 A g ⁻¹)		163
Co ₉ S ₈ @ZnGa ₂ S ₄	1018 C g ⁻¹ at 5 mA cm ⁻²	3 M KOH	–0.05–0.55 V (Hg/HgO)	65% (5–187.5 mA cm ⁻²)	93.5% (10 000)	164
Ni–Co–Mo–S/CNT	1728.6 F g ⁻¹ at 1 A g ⁻¹	2 M KOH	–0.1–0.8 V (Hg/HgO)	55.8% (1–10 A g ⁻¹)		165
HN ₂ CMS	928.1 C g ⁻¹ at 1 A g ⁻¹	3 M KOH	0–0.7 V (Hg/HgO)	52.3% (1–10 A g ⁻¹)	85% (5000)	166
HCCoS@CNT	1250 F g ⁻¹ at 0.5 A g ⁻¹	3 M KOH	0–0.5 V (SCE)	69.6% (1–10 A g ⁻¹)	90.4% (10 000)	167
Co ₃ S ₄ /NiS ₂ /Cu ₂ S	464.16 C g ⁻¹ at 1 A g ⁻¹	6 M KOH	0–0.5 V (Ag/AgCl)			168
CoNi ₂ S ₄ /carbon/MXene	1221.6 F g ⁻¹ at 1 A g ⁻¹	6 M KOH	0–0.6 V (Hg/HgO)	79.1% (1–20 A g ⁻¹)	63.96% (10 000)	40
Ni ₃ S ₄ @Co ₃ S ₄	747.3 C g ⁻¹ at 1 A g ⁻¹	6 M KOH	0–0.6 V (Hg/HgO)	77% (1–10 A g ⁻¹)		169
NiCo ₂ S ₄ /MXene/NC	1786 F g ⁻¹ at 1 A g ⁻¹	3 M KOH	–0.2–0.7 V (Hg/HgO)	52% (1–40 A g ⁻¹)	110.5% (10 000)	170
MoS ₂ /Co ₃ S ₄ /NPC	612 F g ⁻¹ at 1 mV s ⁻¹	1 M KOH	0–0.45 V (Ag/AgCl)		88.59% (9000)	171
Co ₃ S ₄	668 F g ⁻¹ at 1 A g ⁻¹	1 M KOH	0–0.7 V (SCE)	52.8% (1–10 A g ⁻¹)	86.4% (5000)	172
CoNiS	598.8 C g ⁻¹ at 1 A g ⁻¹	6 M KOH	0–0.5 V (Hg/HgO)	59.9% (1–30 A g ⁻¹)	70.1% (10 000)	173
Co ₃ S ₄ –Mo ₁₅ S ₁₉	3283 F g ⁻¹ at 1 A g ⁻¹	2 M KOH	0–0.5 V (Ag/AgCl)	77.7% (1–10 A g ⁻¹)	77% (2500)	174
Au/ZnS@Co ₃ S ₄ @Ni ₃ S ₂	302.6 mA h g ⁻¹ at 1 A g ⁻¹	3 M KOH	0–0.6 V (SCE)	70.3% (1–10 A g ⁻¹)		175
ZnCo ₂ S ₄ @ZIF-67	447.25 F g ⁻¹ at 1 A g ⁻¹	1 M KOH	–0.1–0.6 V (Hg/HgO)	40.3% (1–7 A g ⁻¹)		176
CoNi ₂ S ₄ /C-CNTs	1314.6 C g ⁻¹ at 1 A g ⁻¹	2 M KOH	0–0.6 V (Hg/HgO)	72.1% (1–20 A g ⁻¹)	78% (10 000)	177
P–Co ₃ S ₄ HNCs	499.1 C g ⁻¹ at 1 A g ⁻¹	6 M KOH	0–0.55 V (Hg/HgO)		88.6% (5000)	178
MoS ₂ /CoMoS ₄ /C	426.5 F g ⁻¹ at 1 A g ⁻¹	2 M KOH	0–0.6 V (Hg/HgO)	73.3% (1–20 A g ⁻¹)	93% (10 000)	179
MoNiCo–S	3125.1 F g ⁻¹ at 1 A g ⁻¹	2 M KOH	0–0.7 V (Hg/HgO)	47.6% (1–30 A g ⁻¹)	72.9% (5000)	180
S-hollow ZIF-67 and NiCo-LDH	3744.4 F g ⁻¹ at 1 A g ⁻¹	6 M KOH	–0.2–0.6 V (Hg/HgO)	68.6% (1–10 A g ⁻¹)	82% (3000)	181
Mo–CoS ₂	1382.6 F g ⁻¹ at 0.5 A g ⁻¹	6 M KOH	0–0.7 V (Hg/HgO)	49.0% (0.5–10 A g ⁻¹)	75.75% (1000)	182

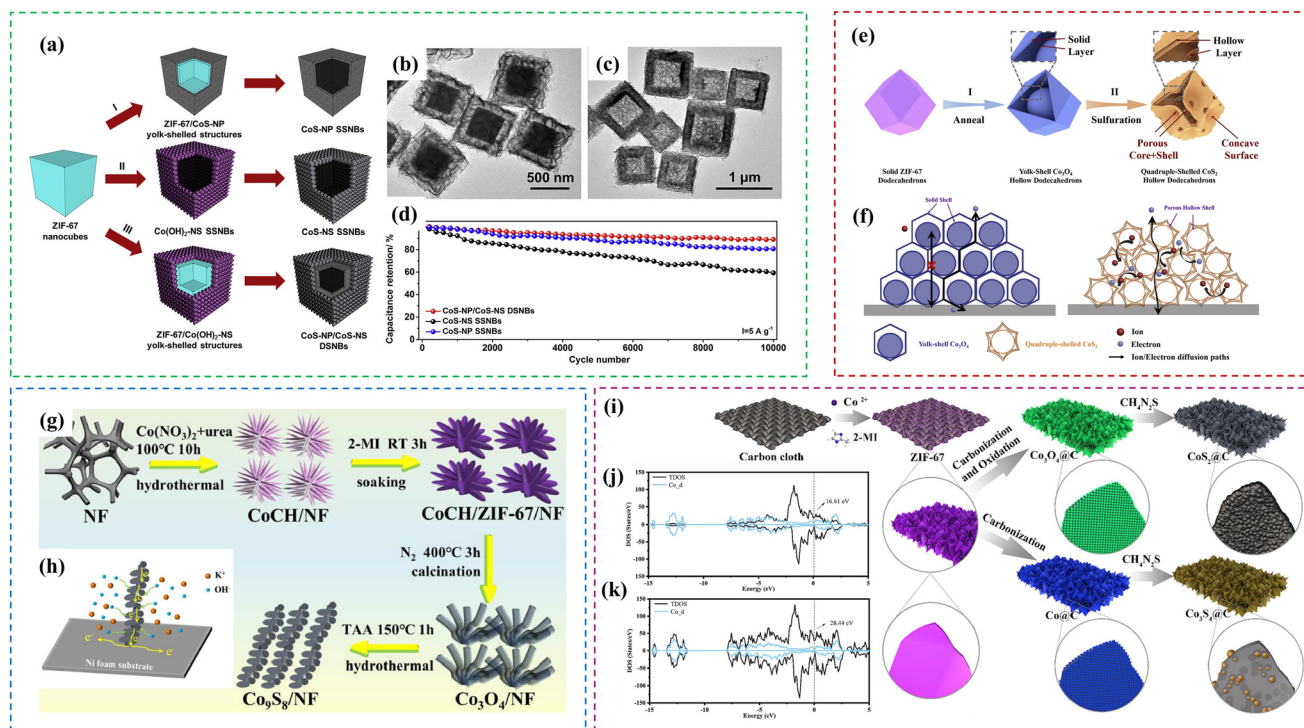
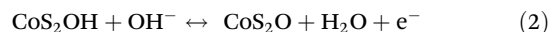
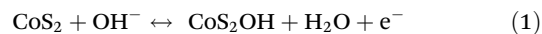


Fig. 9 (a) Procedure for the synthesis of CoS-NP SSNBs, CoS-NS SSNBs and CoS-NP/CoS-NS DSNBs; (b) TEM image of ZIF-67/Co(OH)₂-NS yolk-shell structures; (c) TEM image of CoS-NP/CoS-NS DSNBs; and (d) comparison of the cycling performance of the three CoS nanostructures at 5 A g⁻¹. Reprinted with permission from ref. 114, Copyright 2016, Elsevier Inc. (e) Schematic of the fabrication of quadruple-shelled CoS₂ hollow dodecahedron electrode; (f) schematic of the reasons for the enhanced performance of quadruple-shelled CoS₂ hollow dodecahedrons compared with yolk-shell Co₃O₄ hollow dodecahedrons. Reprinted with permission from ref. 121, Copyright 2019, Elsevier Ltd. (g) Schematic of the synthetic process of Co₉S₈/NF and (h) schematic structure and mechanism of Co₉S₈/NF. Reprinted with permission from ref. 136, Copyright 2021, Elsevier Ltd. (i) Process for the construction of CoS₂ and Co₃S₄ and total density of states (TDOS) of (j) Co₃S₄ and (k) CoS₂. Reprinted with permission from ref. 158, Copyright 2022, Elsevier Ltd.

mation of hierarchical pores and small active powder. Also, it is beneficial to provide a large surface area and short diffusion channels, as shown in Fig. 9h, which can reduce the volume expansion and ensure the stability of the architecture. ZIF-derived Co₉S₈ displayed a large specific capacitance because of its abundant redox sites and high electrical conductivity. The Co₉S₈/NF electrode possessed outstanding electrochemical properties with the specific capacitance of 369.1 mA h g⁻¹ at 1 A g⁻¹ and 75.5% retention at 20 A g⁻¹. After 5000 cycles, it showed 75% capacitance retention at 20 A g⁻¹. Furthermore, a button-type asymmetric supercapacitor (ASC) was assembled with Co₉S₈/NF as the positive electrode, which displayed the maximum specific energy of 48.2 W h kg⁻¹ at the specific power of 799.8 W kg⁻¹ and excellent cycling life with 77% retention of its initial capacitance after 5000 cycles. Wang *et al.*¹⁴⁷ applied chemical vapor deposition (CVD) treatment to obtain a CoS/nitrogen-doped carbon (CoS/NC) composite with a hollow cage-like polyhedron structure formed by the combination of CoS nanosheets and nitrogen-doped carbon skeleton. It exhibited a specific capacitance of 789 F g⁻¹ at a current density of 1 A g⁻¹ and a rate capacity of 80.2% at a current density of 20 A g⁻¹. The CoS/NC-700//AC capacitor showed the highest energy density of 32.8 W h kg⁻¹ when the power density was 620.0 W kg⁻¹ and it retained 89.2% of its

initial capacitance after 10 000 charge-discharge cycles at a current density of 5 A g⁻¹. Meanwhile, Wei *et al.*¹⁵⁸ constructed CoS₂ and Co₃S₄ nanoparticles anchored on a carbon skeleton (CoS₂@C and Co₃S₄@C) depending on if an oxidation process occurred, respectively (Fig. 9i). The reactions are represented by the following equations:



Compared with the inhomogeneous distribution of Co₃S₄@C nanoparticles, a larger specific surface area is provided by numerous CoS₂@C nanoparticles embedded in the 2D carbon skeleton and connected into sheets through effectively morphological construction, which provides more redox channels and active sites for electrochemical reactions. Thus, the CoS₂@C electrode presented a superior electrochemical performance with a high specific capacitance of 1151 F g⁻¹ at 1 A g⁻¹, which is 1.69-times larger than that of Co₃S₄@C. Comparing Fig. 9j and k, density functional theory (DFT) calculations illustrated that CoS₂ can transfer much more charge and has higher electronic activity in the process of OH⁻ adsorption compared with Co₃S₄, proving that CoS₂ has better conductivity. Moreover, an asymmetric supercapacitor was con-

structed using CoS_2 @C//reduced graphene oxide (RGO), which displayed a high energy density of $46.52 \text{ W h kg}^{-1}$ at a power density of 800 W kg^{-1} .

3.2 Multi-metal sulfides

Alternatively, multi-metal sulfides have richer redox-active sites, higher electronic conductivity and synergistic effects between different metal ions. Therefore, numerous studies have been devoted to designing multi-metal sulfides using ZIF-67 as a template. For instance, the Ni ion, similar to the Co ion, is usually used as a dopant ion to obtain multi-metal chalcogenides derived from ZIF-67. Guo *et al.*¹¹⁶ reported the growth of well-aligned NiCo_2S_4 (shown in Fig. 10a–c) and CoS_2 nanoarrays with a hollow/porous configuration on a conductive matrix, which significantly increase the number of electroactive sites, shortened the charge/ion diffusion length, and enhanced the mass/electron transfer. Consequently, the obtained NiCo_2S_4 possessed an excellent specific capacitance of 939 C g^{-1} , a fast charge/discharge rate, and a favorable life span. Similarly, Liu *et al.*¹²⁰ synthesized NiCo_2S_4 hollow nanocages assembled by ultrathin nanosheets through a facile solid-state chemical sulfurization method, as shown in Fig. 10d. Also, as shown in Fig. 10e and f, the obtained hollow NiCo_2S_4 possessed inner cavities and large ultrathin nanosheets for both short ion diffusion distance and rich interfacial active sites, which can dynamically speed up faradaic reactions. A specific capacitance of 1232 F g^{-1} was obtained at a current

density of 2 A g^{-1} for the NiCo_2S_4 electrode. Notably, compared with Co–Ni LDH, as shown in Fig. 10g and h, the NiCo_2S_4 electrode yielded an impressive rate capability and excellent cycling stability (80% capacitance retention after 8000 charge–discharge cycles), mainly due to its robust porous architecture and good electronic conductivity. The aqueous asymmetric supercapacitor assembled with NiCo_2S_4 as the positive electrode also delivered a high energy density of 41.4 W h kg^{-1} at a power density of 689.5 W kg^{-1} . Moreover, Cai *et al.*¹²⁵ changed the order of the sulfidation and cation exchange to obtain CoS_x hollow cages first, and subsequently obtained NiCo_2S_4 by adding Ni^{2+} , as shown in Fig. 10i and j. Compared with CoS_x , as shown in Fig. 10k and l, the NiCo_2S_4 hollow cages exhibited an appealing capacitance of 1382 F g^{-1} at 1 A g^{-1} . Furthermore, asymmetric supercapacitors (ASCs) were fabricated with the synthesized NiCo_2S_4 and active carbon (AC) as the electrodes. The ASCs showed an energy density of 35.3 W h kg^{-1} at a power density of 750 W kg^{-1} and outstanding cycling stability of 79% retention after 10 000 cycles.

In the case of other metal ions, Yang *et al.*¹²² doped Mo in ZIF-67 in the presence of Na_2MoO_4 , and subsequently obtained an Mo-doped CoS hollow nanocage structure (Mo-doped CoS HNC) *via* a sulfurization process. As shown in Fig. 11a–d, the obtained Mo-doped CoS HNC exhibited an enhanced specific capacitance (781.0 F g^{-1} at 0.5 A g^{-1}) compared with the control CoS HNC (387.1 F g^{-1}) and $\text{CoMoO}_4\text{--Co(OH)}_2$ HNC (285.1 F g^{-1}). Furthermore, it also showed a

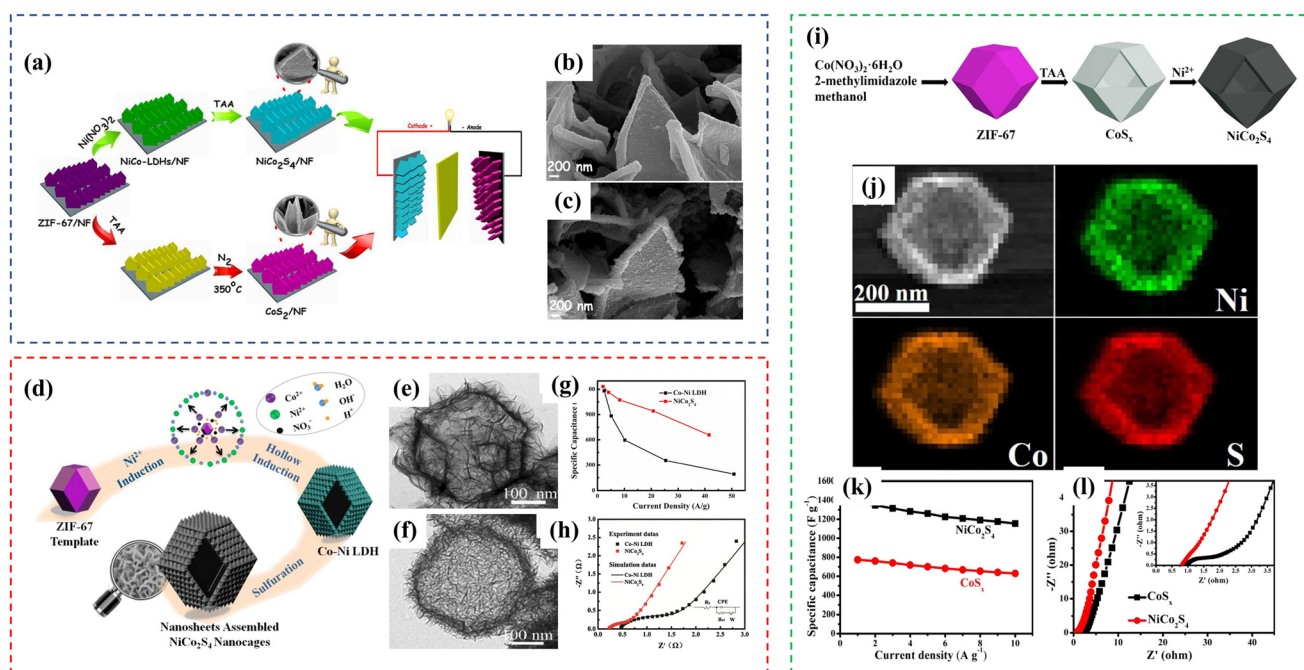


Fig. 10 (a) Schematic of the process for the synthesis of the composite and fabrication of the asymmetric supercapacitor and SEM images of (b) NiCo-LDHs and (c) NiCo_2S_4 . Reprinted with permission from ref. 116, Copyright 2018, the American Chemical Society. (d) Schematic of the fabrication of NiCo_2S_4 ; TEM images of (e) Co–Ni LDH and (f) NiCo_2S_4 ; (g) specific capacitance versus current density and (h) Nyquist plots of Co–Ni LDH and NiCo_2S_4 . Reprinted with permission from ref. 120, Copyright 2019, Springer Nature. (i) Schematic showing the fabrication of NiCo_2S_4 hollow cages; (j) EDS mapping of NiCo_2S_4 ; (k) specific capacitance at different current densities and (l) Nyquist plots of NiCo_2S_4 and CoS_x . Reprinted with permission from ref. 125, Copyright 2019, Elsevier B.V.

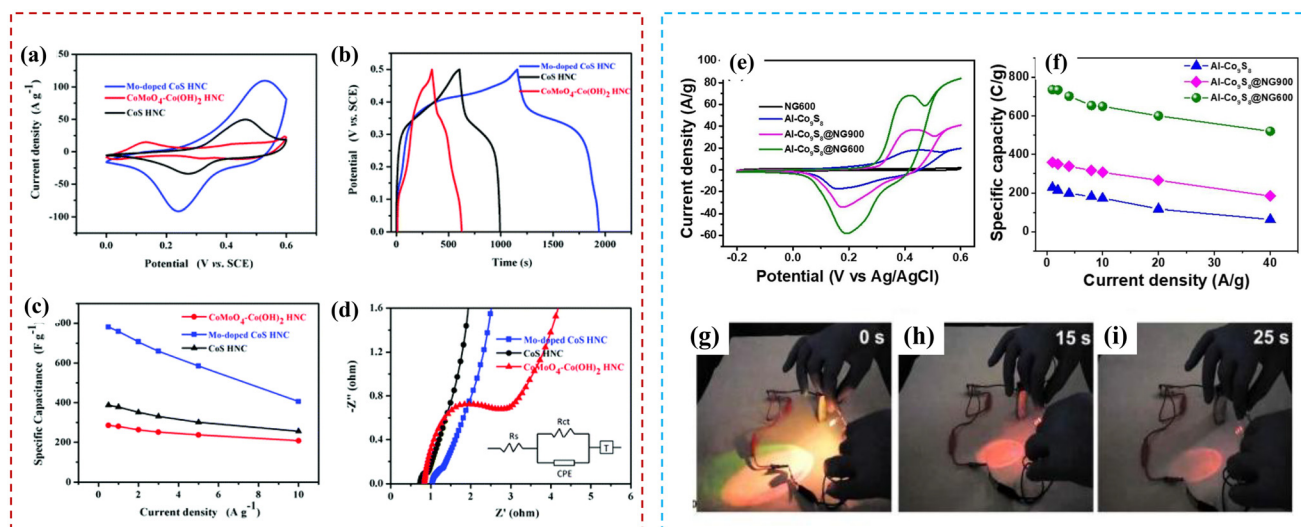


Fig. 11 (a) CV curves, (b) GCD curves, (c) specific capacitance and (d) Nyquist plots of CoS HNC, CoMoO₄-Co(OH)₂ HNC and Mo-doped CoS HNC. Reprinted with permission from ref. 122, Copyright 2019, The Royal Society of Chemistry. (e) CV curves and (f) specific capacitance of NG600, Al-Co₉S₈, Al-Co₉S₈@NG600 and Al-Co₉S₈@NG900; (g–i) photographs of AsSC devices linked in series to light a red LED. Reprinted with permission from ref. 141, Copyright 2021, Elsevier B.V.

superior rate capacity of 52% at a 20-fold increase in current density (10 A g⁻¹). The asymmetric supercapacitor (ASC) device assembled using the Mo-doped CoS HNC as the positive electrode and activated carbon (AC) as the negative electrode displayed a high energy density of 27.7 W h kg⁻¹ at a power density of 799.9 W kg⁻¹ with excellent cycling stability, maintaining 88% of its initial capacitance after 10 000 cycles. The excellent electrochemical performance is attributed to the unique ternary metal sulfide hollow nanocage structure having a large surface area, facile diffusion of ions, good conductivity, and rich redox reactions as well as the synergistic effect between Mo and Co ions. Also, Zhao *et al.*¹²⁶ presented the synthesis and characterization of ZIF-67-derived mesoporous copper cobalt sulfide (CuCo₂S₄) prepared *via* simple reflux and solvothermal reactions. The obtained CuCo₂S₄ electrode showed a high specific capacity of up to 672 C g⁻¹ (1344 F g⁻¹) at 1 A g⁻¹. Additionally, Goda *et al.*¹⁴¹ reported Al doping to improve the conductivity of cobalt sulfide. A novel type of core/shell architecture was successfully designed from aluminum-doped cobalt sulfide encapsulated by nitrogen-doped graphene (Al-doped Co₉S₈@NG) through the solvothermal/sulfuration of the ZIF-67 structure, subsequent wrapping with a PPy layer and calcination in argon gas at various temperatures. Interestingly, integrating the morphology and composition merits endowed the Al-doped Co₉S₈@NG600 electrode with highly enhanced supercapacitive features, as shown in Fig. 11e and f. The electrode attained a superior specific capacity of about 736 C g⁻¹ at an applied current density of 1 A g⁻¹, ultra-long cycle stability of 92% after 10 000 cycles, and a remarkable retention rate (71%). Subsequently, a solid-state AsSC device with Al-doped Co₉S₈@NG core/shell as the positive electrode and activated PANI-derived carbon nanorods (ACNRs) as the negative electrode was assembled. The device exhibited

outstanding specific capacitance, energy density, and power density values of 134 F g⁻¹, 53.3 W h kg⁻¹, and 0.954 kW kg⁻¹, respectively, with a considerable cycle life stability of 93% after consuming 10 000 cycles. Further, when two AsSC devices were linked in series, a multicolor LED could be lit for 25 s, demonstrating their availability for making modern portable electronics, as shown in Fig. 11g–i.

3.3 Composite materials

As mentioned, ZIF-67-derived sulfides usually exhibit the drawbacks of limited rate capability and poor cyclic stability. Accordingly, composite materials are being developed as promising electrode materials because rationally designed structures can improve the cycling stability and rate capability and facilitate electronic transport in electrodes.⁴² Jian *et al.*¹¹⁷ designed a hybrid structure of a cobalt sulfide nanocage derived from ZIF-67 and interconnected by carbon nanotubes (CNT/CoS). The carbon nanotube/ZIF-67 (CNT/ZIF-67) nanocomposites with controlled ZIF-67 particle sizes were systematically studied by varying the mass ratio of CNTs to ZIF-67 during crystallization, followed by subsequent sulfurization with thioacetamide (Fig. 12a). Benefiting from the porous nanocage architecture and conductive CNTs, the optimized CNT/CoS nanocage exhibited an excellent electrochemical performance with an outstanding specific capacitance (2173.1 F g⁻¹ at 5 A g⁻¹) and high rate capability (65% retention at 20 A g⁻¹), as shown in Fig. 12b and c. More importantly, the fabricated symmetric supercapacitor exhibited an energy density of 23.3 W h kg⁻¹ at a power density of 3382.2 W kg⁻¹ and impressive long-term stability (96.6% retention after 5000 cycles). Additionally, Zhou *et al.*¹⁴⁰ constructed hollow tube@sheet NiCo₂S₄ core-shell nanoarrays by *in situ* growing ZIF-67 on Co-precursor nanorod arrays and sequentially performing

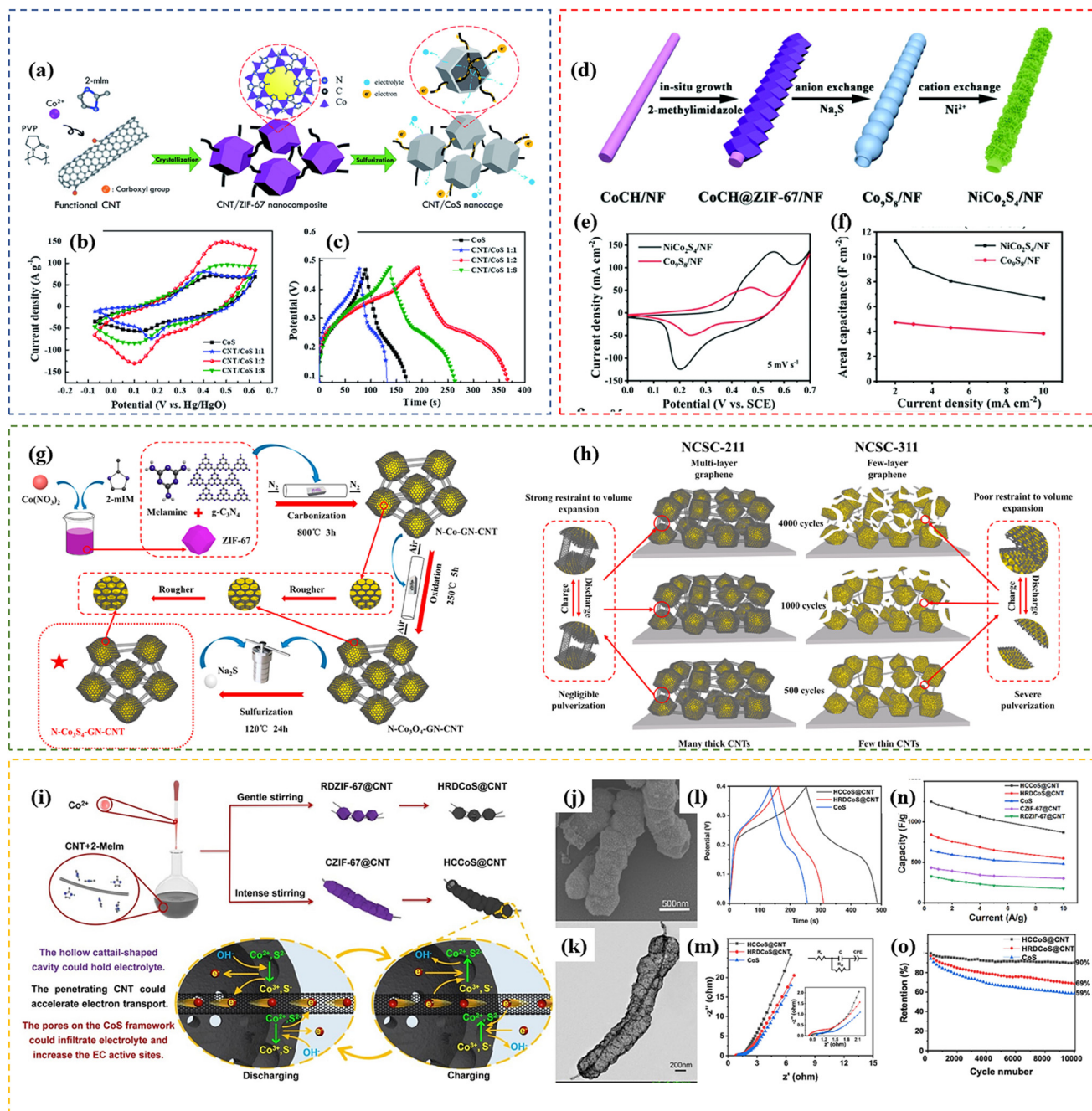


Fig. 12 (a) Schematic of the synthesis of hybrid CNT/CoS nanocages; (b) CV curves at 100 mV s⁻¹ and (c) GCD curves at 5 A g⁻¹ for CoS, CNT/CoS (1:1), CNT/CoS (1:2) and CNT/CoS (1:8). Reprinted with permission from ref. 117, Copyright 2019, The Royal Society of Chemistry. (d) Synthetic procedure for NiCo₂S₄/NF; (e) CV curves at 5 mV s⁻¹ and (f) specific capacitance of Co₉S₈/NF and NiCo₂S₄/NF. Reprinted with permission from ref. 140, Copyright 2021, The Royal Society of Chemistry. (g) Schematic diagram of the construction of N-Co₉S₄-GN/CNT nanostructure and (h) schematic of the nanostructure changes in NCSC-211 and NCSC-311 after 500, 1000 and 4000 cycles. Reprinted with permission from ref. 149, Copyright 2022, Elsevier Ltd. (i) Schematic representation showing the various synthesis procedures for generating CoS@CNT structures and the electrochemical process occurring on hierarchical pore-structured HCCoS@CNT. Gentle stirring resulted in the formation of HRDCoS@CNT with a rhombic dodecahedron-shaped morphology by controlling the stirring speed to 200 rpm, while intense stirring resulted in the fabrication of HCCoS@CNT with a cattail-shaped morphology by controlling the stirring speed at 1000 rpm. (j) SEM image and (k) TEM image of HCCoS@CNT and (l) GCD curves at 2 A g⁻¹, (m) Nyquist plots, (n) specific capacitance and (o) cycling stability at 10 A g⁻¹ of CoS, HCCoS@CNT and HRDCoS@CNT. Reprinted with permission from ref. 167, Copyright 2023, Elsevier B.V.

anion-exchange (S^{2-}) and cation-exchange (Ni^{2+}) (Fig. 12d). The well-defined nanostructures could shorten the ion transport path in the charging-discharging process and increase the specific surface area and electrochemical active sites, improving the electrochemical performance. Therefore, the unique tube@sheet NiCo_2S_4 core-shell nanoarrays exhibited an intriguing electrochemical performance and showed an excellent areal capacitance of 11.3 F cm^{-2} (3227.94 F g^{-1}) at a current density of 2 mA cm^{-2} (2 A g^{-1}) (Fig. 12e and f). The assembled asymmetric supercapacitor device delivered a high energy density of $0.42 \text{ mW h cm}^{-2}$ at a power density of 2.1 mW cm^{-2} and displayed outstanding cyclic stability (90.2% retention after 5000 cycles). Similarly, Zhang *et al.*¹⁴⁹ proposed a ZIF-67 derived, nitrogen-doped, graphene-coated and carbon nanotube-interlinked 3D $\text{Co}_3\text{S}_4/\text{C}$ conductive network (N- $\text{Co}_3\text{S}_4\text{-GN/CNT}$), as shown in Fig. 12g, for high-performance supercapacitors. By controlling the mass ratio of ZIF-67, melamine and $\text{g-C}_3\text{N}_4$, various microstructures with determined electrochemical performances could be achieved. The nanocomposites synthesized with the component mass ratio of 2 : 1 : 1 (NCSC-211) were proven to have the most excellent comprehensive electrochemical properties, as shown in Fig. 12h. In the NCSC-211 nanostructure, multi-layer graphene functions as conductive shells for improving the cycling performance by alleviating the pulverization caused by volume change, the thick CNTs act as conductive bridges and agglomeration spacers, which increase the electron conductivity and provide more active sites for redox reaction, and doped-nitrogen offers enhanced electrolyte wettability and faster electron transfer. Consequently, the NCSC-211 electrode displayed a specific capacitance of 1158 F g^{-1} at 1 A g^{-1} , rate capability of 86% at 10 A g^{-1} and extraordinary cycling stability with 97.2% capacitive retention after 4000 cycles. Moreover, Li *et al.*¹⁶⁵ demonstrated the synthesis of Mo-ZIF-67/CNT composites through mechanical stirring and co-precipitation. After that, Ni, Co and Mo trimetallic sulfide/CNT composites (Ni-Co-Mo-S/CNT) were produced through further ion exchange/etching and vulcanization processes. The material had multiple valence states of three different metal ions, providing a large number of oxidation-reduction sites. The doping of CNTs endowed it with a unique coral-like structure, which helped to form its huge specific surface area and large mesopores. The electrode exhibited an impressive performance with a specific capacitance of 1728.6 F g^{-1} at a current density of 1 A g^{-1} . It also had a good rate capability, maintaining 55.8% of its specific capacitance when the current density increased tenfold. Moreover, Yan *et al.*¹⁶⁷ developed an *in situ* self-assembly strategy to prepare hollow composites using ZIF-67 and carbon nanotubes, and subsequently converted ZIF-67 to cobalt sulfide *via* a sulfurization strategy (Fig. 12i). The unique hollow composites with different dimensions, as shown in Fig. 12j and k, exhibited a synergistic effect between subunits, resulting in excellent electrochemical properties. The impact of particle cavity channel size on electrochemical properties was evaluated systematically. As a result, the obtained CoS@CNT with hollow cattail-shape structures (HCCoS@CNT) exhibited a

high specific capacitance (1250 F g^{-1}) and cyclic stability (90.4% for over 10 000 cycles at 10 A g^{-1}) (as shown in Fig. 12l-o).

Besides carbon nanotubes, graphene is also a good conductive carbon material for improving the electrochemical properties of ZIF-67-derived transition metal sulfides. Wu *et al.*¹³³ reported the preparation of a sandwich-like $\text{GO/CoS}_x\text{-rGO/GO}$ hybrid film *via* a three-step process and the resulting $\text{rGO/CoS}_x\text{-rGO/rGO}$ hybrid film was shown to have a good electrochemical performance because it combined the good pseudocapacitor property of cobalt sulfide and good conductivity and electric double layer capacitor property of rGO. Similarly, Reddy *et al.*¹⁶² added a calcination process and obtained $\text{CoS}_2\text{@gC/rGO}$ by CVD treatment, as shown in Fig. 13a. The $\text{CoS}_2\text{@gC/rGO}$ composite exhibited a specific capacitance of 1188 F g^{-1} , cyclic stability of 76% and 99% coulombic efficiency (Fig. 13b-d). An all-solid-state asymmetric supercapacitor device was fabricated with $\text{CoS}_2\text{@gC/rGO}$ and hydrothermally reduced graphene oxide (hrGO) as the positive and negative electrodes, respectively. The device exhibited a high specific capacitance of 233 F g^{-1} at a current density of 1.5 A g^{-1} and delivered a high energy density of $82.88 \text{ W h kg}^{-1}$ at a power density of $1199.56 \text{ W kg}^{-1}$. Particularly, the device conserved an energy density of $42.44 \text{ W h kg}^{-1}$ even at a high-power density of 7999.9 W kg^{-1} . Additionally, it showed good cyclic stability after 10 000 cycles of repeated charging/discharging, suggesting its potential for practical supercapacitor applications. Moreover, Wu *et al.*¹⁶¹ designed the $\text{rGO/NiCo}_2\text{S}_4$ material by using GO and ZIF-67 as the template and precursor, which increased the specific surface area and provided active sites for redox reactions and shortened ion transport pathways. The synthesized $\text{rGO-10/NiCo}_2\text{S}_4$ exhibited excellent electrochemical properties as an electrode material, which had a high specific capacity of 171 mA h g^{-1} and $121.9 \text{ mA h g}^{-1}$ (1 A g^{-1} and 10 A g^{-1}). The as-obtained $\text{rGO-10/NiCo}_2\text{S}_4\text{//AC}$ asymmetric supercapacitor (ASC) delivered a power density of 870 W kg^{-1} at the specific energy of 41 W h kg^{-1} , with 88.2% capacitance retention after 5000 cycles at 5 A g^{-1} .

As a representative member of the emerging 2D MXenes, $\text{Ti}_3\text{C}_2\text{T}_x$ -based supercapacitor materials have been comprehensively reviewed and demonstrated to be beneficial for the conductivity and the structural stability of ZIF-67-derived transition metal sulfides.¹⁸³ For example, Ruan *et al.*¹³⁷ synthesized Ti_3C_2 MXene-wrapped CoNi_2S_4 nanosheets grown on nickel foam, as shown in Fig. 14a and b, which delivered a very high specific capacity of 933 C g^{-1} at 1 A g^{-1} and good rate performance (Fig. 14c) due to the fact that the unique dendrite morphology can provide many exposed electro-active sites and the wrapped conductive MXene can facilitate charge transfer. An asymmetric supercapacitor was assembled using $\text{CoNi}_2\text{S}_4/\text{MXene/NF}$ and RGO as positive and negative electrodes, respectively, which delivered a high energy density of 30.5 W h kg^{-1} without deteriorating its high power density (1587 W kg^{-1}). Also, Luo *et al.*¹⁴⁴ obtained $\text{Co}_3\text{S}_4/\text{Ti}_3\text{C}_2\text{T}_x$ powder by hydrothermal reaction and the electrode containing $\text{Co}_3\text{S}_4/\text{Ti}_3\text{C}_2\text{T}_x$ as the active material exhibited a very high specific

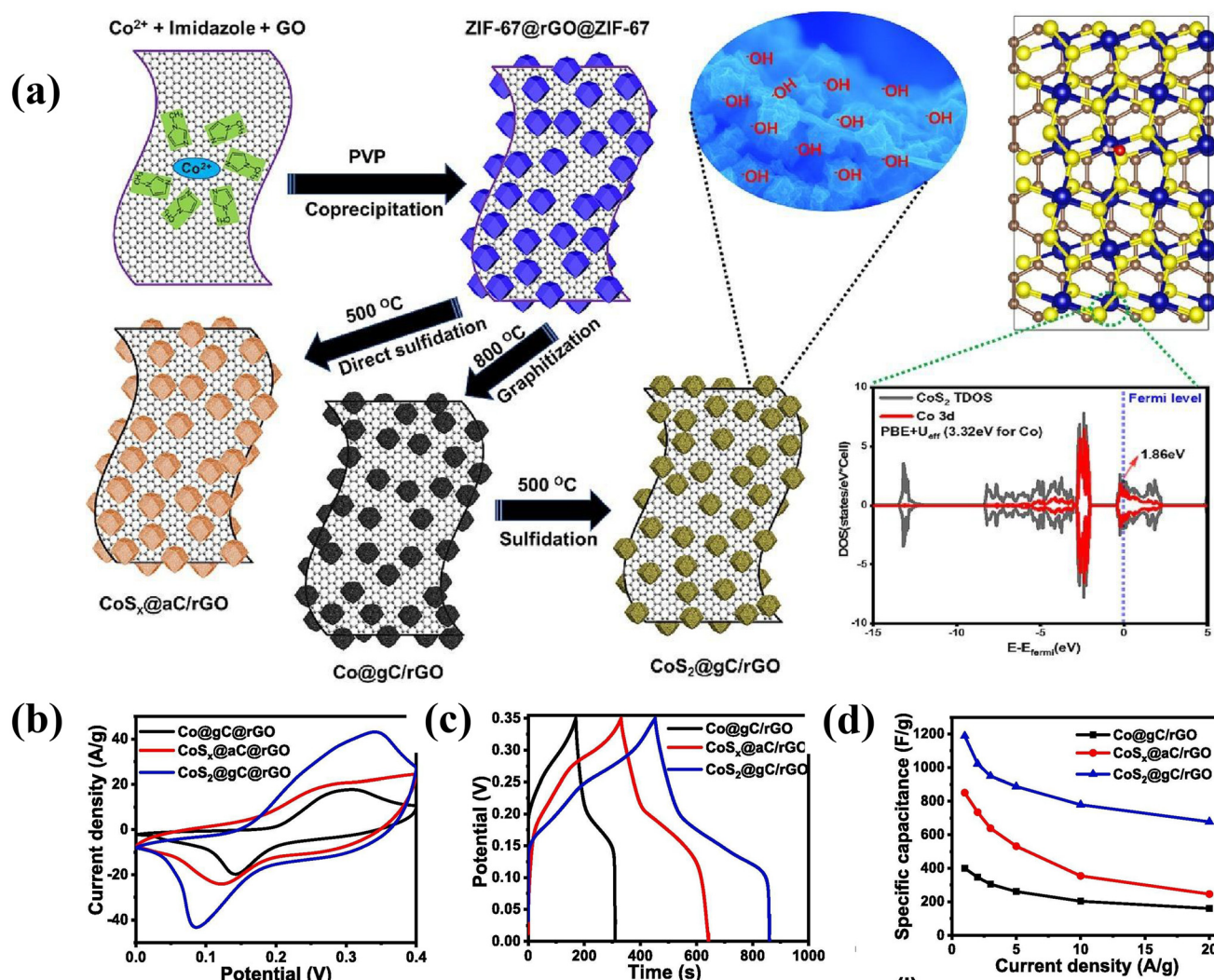


Fig. 13 (a) Schematic of the synthesis of $\text{CoS}_2\text{@gC/rGO}$, the insert is optimized configuration of $\text{CoS}_2(200)$ and total density of states (TDOS) with Co 3d contributions of CoS_2 (blue and yellow colors represent Co and S atoms, respectively); and (b) CV curves at 25 mV s^{-1} , (c) GCD curves at 1 A g^{-1} and (d) specific capacitance of Co@gC/rGO , $\text{CoS}_x\text{@aC/rGO}$ and $\text{CoS}_2\text{@gC/rGO}$. Reprinted with permission from ref. 162, Copyright 2023 Elsevier B.V.

capacitance of 602 F g^{-1} at 1 A g^{-1} , which was 2.6-times higher than of the ZIF-67/ $\text{Ti}_3\text{C}_2\text{T}_x$ -containing electrode. The supercapacitor based on $\text{Co}_3\text{S}_4/\text{Ti}_3\text{C}_2\text{T}_x$ maintained 81.6% of its original capacitance even at a current density of 10 A g^{-1} . Thus, the introduction of $\text{Ti}_3\text{C}_2\text{T}_x$ in ZIF-67 not only improved the electrical conductivity of the hybrid material but also its structural stability, which acted as a support. The asymmetric $\text{Co}_3\text{S}_4/\text{Ti}_3\text{C}_2\text{T}_x\text{//AC}$ supercapacitor (ASC) containing activated carbon (AC) as the anode showed a high energy density of 44.9 W h kg^{-1} at a power density of 800.3 W kg^{-1} . This ASC also demonstrated a high rate performance (79.2%) and excellent cycling stability (with 88.3% capacitance retention and 99.23% coulombic efficiency after 5000 cycles). Similarly, Qi *et al.*¹⁵³ reported that $\text{CoNi}_2\text{S}_4/\text{MXene}$ derived from ZIF-67/MXene and NiCo-LDH/MXene exhibited an outperforming specific capacitance (751 C g^{-1} at 1 A g^{-1}), which was much higher than that of pure CoNi_2S_4 (600 C g^{-1} at 1 A g^{-1}). An asymmetric super-

capacitor ($\text{CoNi}_2\text{S}_4/\text{MXene}\text{//reduced graphene oxide (RGO)}$) was assembled, which delivered a high energy density of 33.8 W h kg^{-1} and excellent cycling performance. As shown in Fig. 14d, Jiao *et al.*⁴⁰ added a carbonization process to improve the conductivity and structural stability of the obtained $\text{CoNi}_2\text{S}_4/\text{carbon/MXene}$ (Fig. 14e). $\text{CoNi}_2\text{S}_4/\text{carbon/MXene}$ exhibited the specific capacitance of 1221.6 F g^{-1} ($169.7 \text{ mA h g}^{-1}$) at 1 A g^{-1} and still maintained a high capacitance of 966.4 F g^{-1} ($134.2 \text{ mA h g}^{-1}$) at 20 A g^{-1} (79.1% of the former), with a better cycling stability compared with other electrodes, as shown in Fig. 14f. After assembling it with activated carbon into an asymmetric supercapacitor, the device delivered a high energy density of $19.82 \text{ W h kg}^{-1}$ at a power density of 469.31 W kg^{-1} and maintained about 71.17% of its initial capacitance after 30 000 cycles at a current density of 20 A g^{-1} , representing excellent cycle stability and rate capability. Moreover, Li *et al.*¹⁷⁰ fabricated hierarchical hollow core-shell microspheres

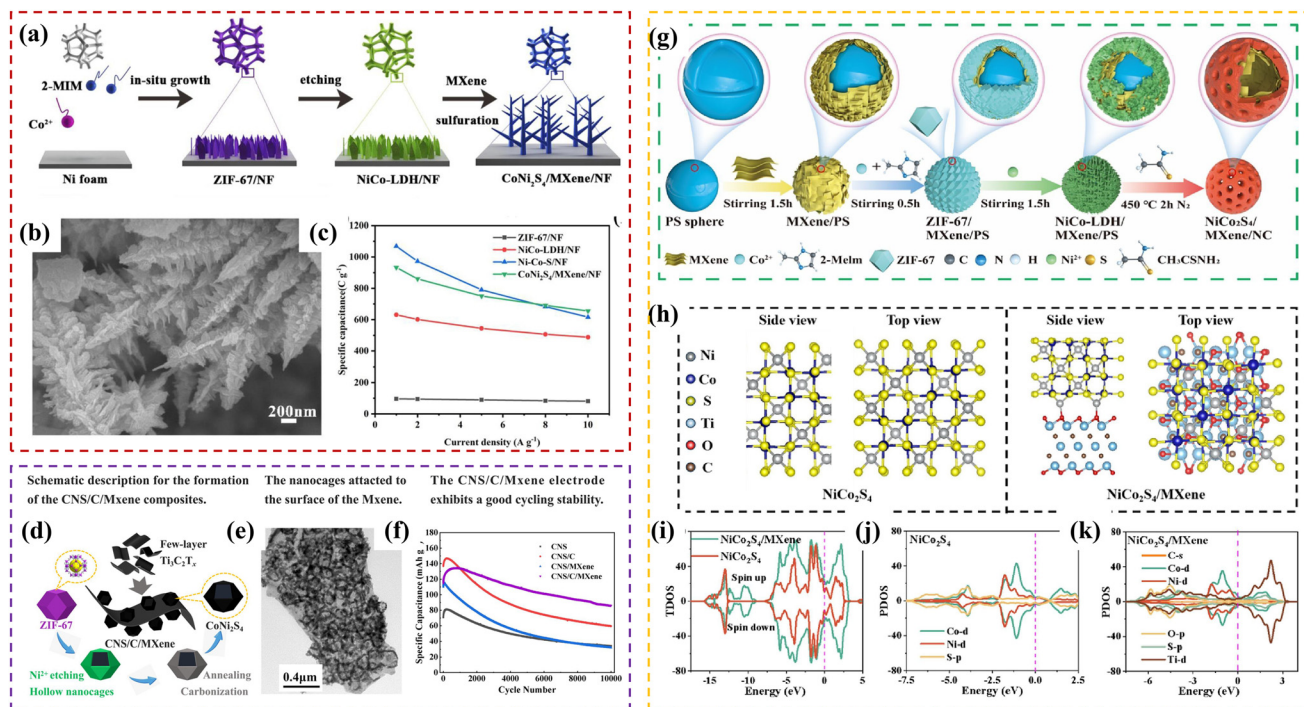


Fig. 14 (a) Schematic of synthetic process for dendrite $\text{CoNi}_2\text{S}_4/\text{MXene}/\text{NF}$; (b) SEM image of $\text{CoNi}_2\text{S}_4/\text{MXene}/\text{NF}$; and (c) specific capacitance of ZIF-67/NF, NiCo-LDH/NF, Ni-Co-S/NF and $\text{CoNi}_2\text{S}_4/\text{MXene}/\text{NF}$. Reprinted with permission from ref. 137, Copyright 2021, Elsevier B.V. (d) Schematic description of the formation of the CNS/C/MXene composites; (e) TEM images of CNS/C/MXene; and (f) cycling stability of CNS, CNS/C, CNS/MXene and CNS/C/MXene. Reprinted with permission from ref. 40, Copyright 2024, Elsevier Ltd. (g) Schematic diagram of the preparation of $\text{NiCo}_2\text{S}_4/\text{MXene}/\text{C}$; (h) constructed models of NiCo_2S_4 and $\text{NiCo}_2\text{S}_4/\text{MXene}$ for calculation; (i) TDOS of NiCo_2S_4 and $\text{NiCo}_2\text{S}_4/\text{MXene}$; and PDOS of (j) NiCo_2S_4 and (k) $\text{NiCo}_2\text{S}_4/\text{MXene}$. Reprinted with permission from ref. 170, Copyright 2024, Elsevier B.V.

of $\text{NiCo}_2\text{S}_4/\text{MXene}/\text{N}$ -doped carbon ($\text{NiCo}_2\text{S}_4/\text{MXene}/\text{NC}$) using dual templates of polyethylene microspheres and ZIF-67 (Fig. 14g). The integration of MXene and N-doped carbon significantly enhanced the electronic conductivity of the electrode, while the construction of hollow spherical structures effectively alleviated the instability of $\text{NiCo}_2\text{S}_4/\text{NC}$ during the charge–discharge cycles, leading to an excellent charge storage performance with a high specific capacitance (1786 F g^{-1} at 1 A g^{-1}) and impressive cycling stability (over 100% capacitance retention after 10 000 cycles). The corresponding hybrid supercapacitor displayed a high specific capacitance (190 F g^{-1} at 1 A g^{-1}) with a maximum energy density of 67 W h kg^{-1} at 796 W kg^{-1} and great cycling stability (over 80% capacitance retention after 10 000 cycles). As shown in Fig. 14h–k, density functional theory (DFT) calculations revealed that addition of MXene enhanced the conductivity of NiCo_2S_4 .

Cheng *et al.*³⁷ inlaid Co_3S_4 hollow nanocages (HNCs) derived from ZIF-67 on polypyrrole (PPy) tubes, forming a $\text{Co}_3\text{S}_4\text{-HNCs}@PPy$ hybrid with intertwined “ $\text{Co}_3\text{S}_4\text{-to-PPy-to-PPy-to-PPy}$ ” conductive networks *via* a facile solution method. The as-synthesized $\text{Co}_3\text{S}_4\text{-HNCs}@PPy$ showed outstanding electrochemical activity (1706 F g^{-1} at 1 A g^{-1}) together with a high rate capability (73.2% retention at 10 A g^{-1}), which was significantly superior to individual $\text{Co}_3\text{S}_4\text{-HNCs}$, PPy or a physical mixture of Co_3S_4 and PPy. Remarkably, the asymmetric super-

capacitor based on $\text{Co}_3\text{S}_4\text{-HNCs}@PPy$ delivered a high energy density of 50.5 W h kg^{-1} (at 849.1 W kg^{-1}) with high durability (82.8% retention after 10 000 cycles). The outstanding supercapacitor property can be attributed to the synergistic advantages of the intertwined “ $\text{Co}_3\text{S}_4\text{-to-PPy-to-PPy}$ ” networks including rich reactive sites, shortened charge diffusion pathway and enhanced charge transfer and mechanical stability. Similarly, Zhao *et al.*¹³⁴ grew the ZIF-67-derived porous CoNi_2S_4 on intercrosslinked PPy tubes to obtain the $\text{NiCoS}@PPy$ hybrid *via* a solution sulfidation (as shown in Fig. 15a). The $\text{NiCoS}@PPy$ electrode achieved an ultrahigh specific capacitance of 2316.6 and 1409.5 F g^{-1} at 1 and 10 A g^{-1} , largely outperforming the control NiCoS or NiCo-LDH@PPy (Fig. 15b–d). Furthermore, the fabricated ASC utilizing $\text{NiCoS}@PPy$ as the cathode displayed an outstanding energy storage capability (34.4 W h kg^{-1} at 799 W kg^{-1}) and splendid cyclic life (retaining 84% initial capacitance after 8500 cycles). Additionally, Wu *et al.*¹⁴⁵ initially assembled ZIF-67 on carbon cloth, which was further hydrothermally converted to Co_9S_8 , and subsequently PPy was coated on the surface of $\text{CC}/\text{Co}_9\text{S}_8$ *via* an electrodeposition process. The obtained $\text{CC}/\text{Co}_9\text{S}_8/\text{PPy}$ electrode showed 83.5% capacity retention after 2500 charge–discharge cycles due to the buffered volume change of Co_9S_8 during the redox process by the introduction of the PPy shell. Moreover, Xu *et al.*¹³² used polyaniline (PANI) as a growth substrate for ZIF-67 as a transfer

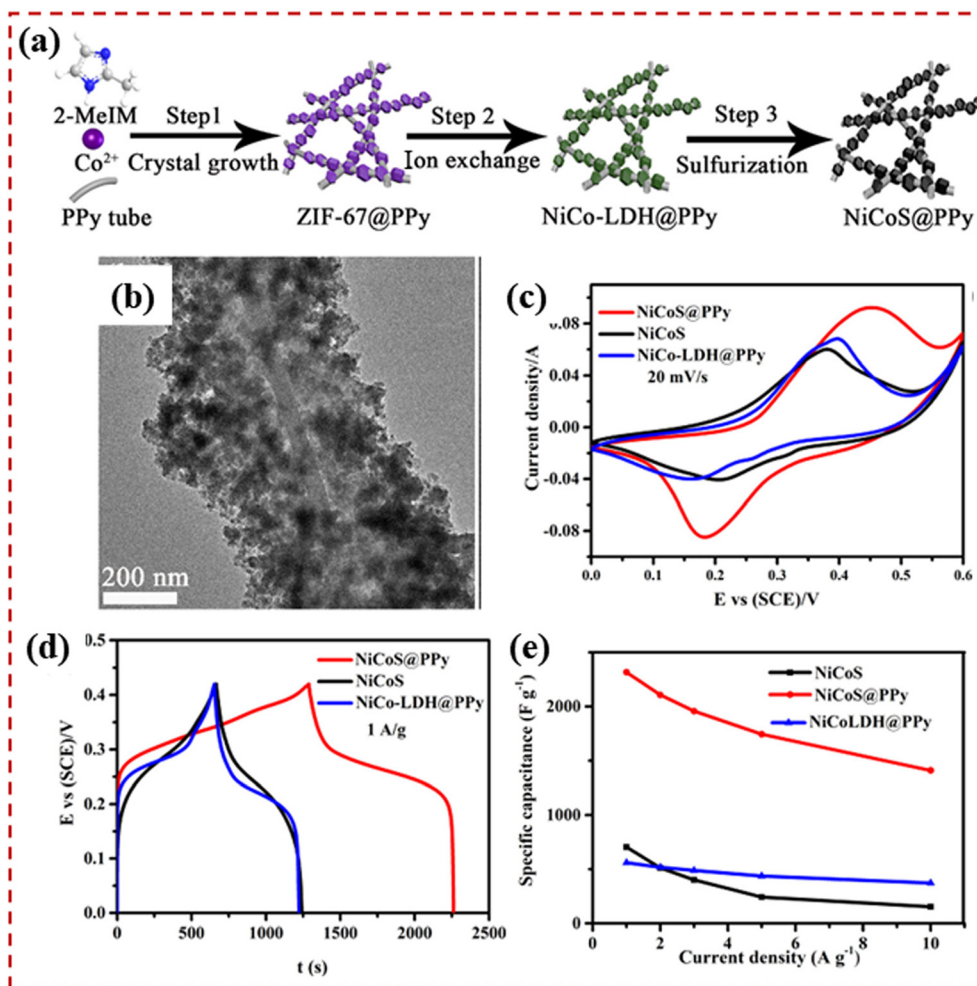


Fig. 15 (a) Procedure for the preparation of porous NiCoS@PPy; (b) TEM image of NiCoS@PPy; (c) CV curves at 20 mV s⁻¹, (d) GCD curves at 1 A g⁻¹ and (e) specific capacitance of NiCoS, NiCo-LDH@PPy and NiCoS@PPy. Reprinted with permission from ref. 134, Copyright 2021, the American Chemical Society.

scaffold of electrons and worked as a wire to connect nanoparticles, improving the conductivity of ZIF-67. The sulfides (Co₃S₄/PANI) obtained by sulfurization exhibited a high specific capacitance of up to 11 times that of ZIF-67 at 1 A g⁻¹. Also, the assembled asymmetric supercapacitors (ASC) device exhibited a high specific energy of 40.75 W h kg⁻¹ at a specific power of 800 W kg⁻¹ and displayed super cycling stability. After 20 000 cycles of charge and discharge tests, it still maintained 88% of its initial capacitance at a higher current density of 5 A g⁻¹.

Combining ZIF-67-derived transition metal sulfides with other compounds is an effective strategy to improve their electrochemical performance by taking advantage of their synergistic effect. Hou *et al.*¹¹⁵ successfully fabricated a core-shell-structured Co₉S₈@N-C@MoS₂ nanocube through a sulfurization process based on ZIF. Due to their improved electrical conductivity and large surface area, the Co₉S₈@N-C@MoS₂ nanocubes with a core-shell heterostructure exhibited a better electrochemical performance in supercapacitors

compared with Co₉S₈ and delivered a high specific capacitance of 410 F g⁻¹ at the current density of 10 A g⁻¹ after 20 000 cycles with excellent cycling stability (101.7% of the initial value). Similarly, Saha *et al.*¹⁷⁴ used ZIF-67 and Mo-precursor to obtain Co₃S₄-Mo₁₅S₁₉ (CMS/NF) *via* one-pot hydrothermal sulfurization (Fig. 16a). The unique stellate-shaped architecture of the CMS/NF microflowers enhanced the exposure of the redox active sites, improving the charge storage and exhibiting superior performance. On account of the synergy of the metal ions and stellate-shaped hierarchical architecture, the CMS/NF hybrid sulfide showed an excellent specific capacitance value of 3283 F g⁻¹ at a current density of 1 A g⁻¹ with a capacitance retention of 77.7% at 10 A g⁻¹. The asymmetric supercapacitor device based on CMS/NF hybrid sulfide with aqueous KOH electrolyte exhibited a high specific energy of 40.8 W h kg⁻¹ at 400 W kg⁻¹ with excellent cycling life of 81% after 5000 cycles with ~100% coulombic efficiency. Also, according to the total density of states, as shown in Fig. 16b and c, it was concluded that compared to

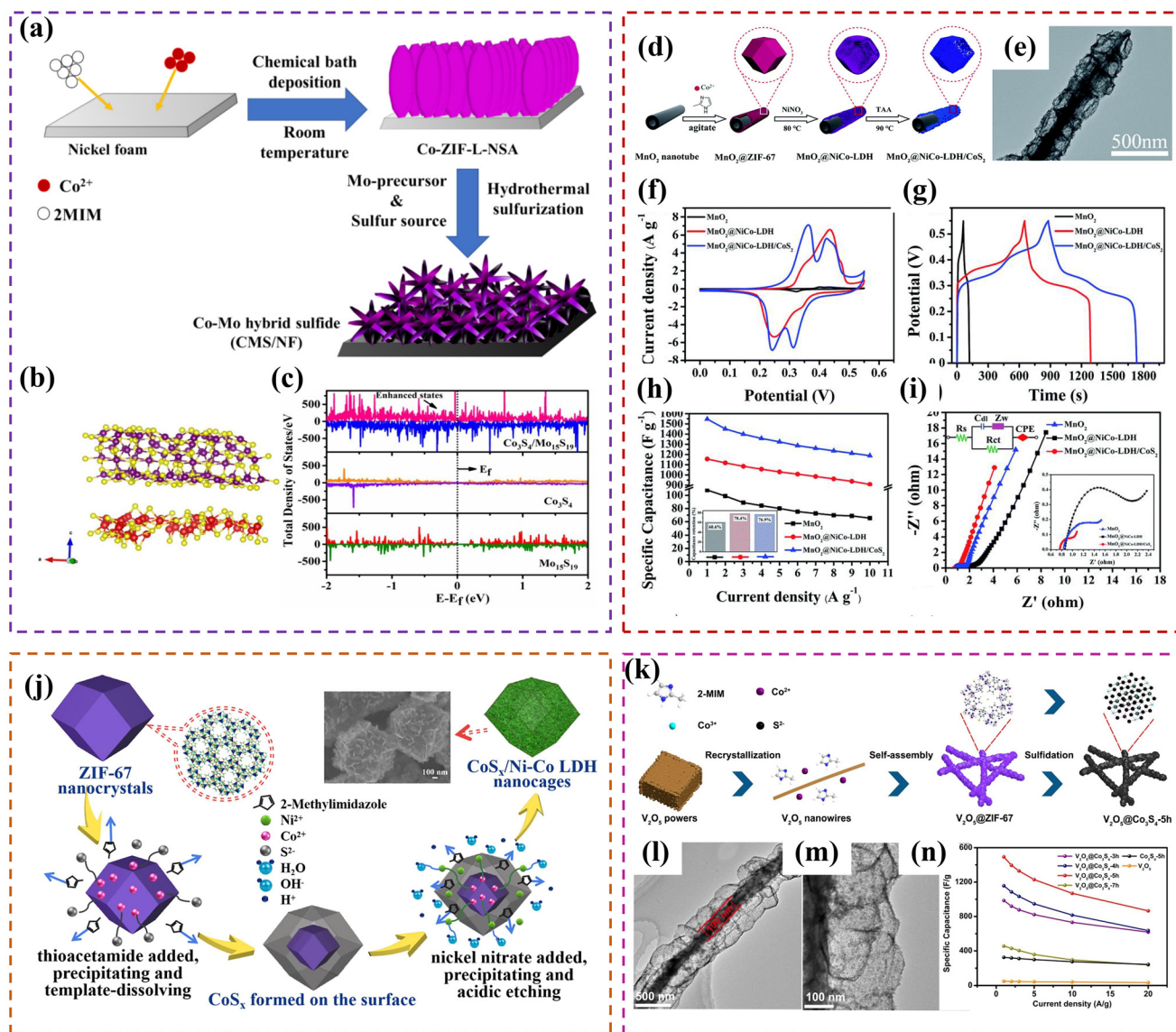


Fig. 16 (a) Schematic of the synthesis process for CMS/NF; (b) DFT optimized structure of $\text{Co}_3\text{S}_4\text{-Mo}_{15}\text{S}_{19}$, where red, violet, and yellow colour represent Mo, Co, and S atoms, respectively; and (c) total density of states for (i) pristine $\text{Mo}_{15}\text{S}_{19}$, (ii) pristine Co_3S_4 , and (iii) $\text{Co}_3\text{S}_4\text{-Mo}_{15}\text{S}_{19}$ hybrid structure. Reprinted with permission from ref. 174, Copyright 2024, Elsevier Ltd. (d) Schematic diagram of the synthesis of $\text{MnO}_2\text{@NiCo-LDH/CoS}_2$; (e) TEM image of $\text{MnO}_2\text{@NiCo-LDH/CoS}_2$; (f) CV curves at 1 mV s^{-1} , (g) GCD curves at 1 A g^{-1} , (h) specific capacitance and (i) Nyquist plots of MnO_2 , $\text{MnO}_2\text{@NiCo-LDH}$ and $\text{MnO}_2\text{@NiCo-LDH/CoS}_2$. Reprinted with permission from ref. 119, Copyright 2019, The Royal Society of Chemistry. (j) Schematic illustration of the fabrication process of $\text{CoS}_x\text{/Ni-Co LDH}$ nanocages. Reprinted with permission from ref. 123, Copyright 2019 Elsevier B. V.; (k) schematic diagram showing the construction of $\text{V}_2\text{O}_5\text{@Co}_3\text{S}_4$; (l and m) TEM images of $\text{V}_2\text{O}_5\text{@Co}_3\text{S}_4$; and (n) specific capacitance of the V_2O_5 , Co_3S_4 -5 h, $\text{V}_2\text{O}_5\text{@Co}_3\text{S}_4$ -3 h, $\text{V}_2\text{O}_5\text{@Co}_3\text{S}_4$ -4 h, $\text{V}_2\text{O}_5\text{@Co}_3\text{S}_4$ -5 h and $\text{V}_2\text{O}_5\text{@Co}_3\text{S}_4$ -7 h at $1\text{--}20 \text{ A g}^{-1}$. Reprinted with permission from ref. 152, Copyright 2022, Elsevier B.V.

the pristine structures, the hybrid system had enhanced states close to the Fermi level, confirming the improvement in conductivity.

Wang *et al.*¹¹⁹ designed new one-dimensional hierarchical hollow nickel-cobalt layered double hydroxide nanocages assembled on MnO_2 nanotubes with uniformly dispersed CoS_2 nanoparticles, $\text{MnO}_2\text{@NiCo-LDH/CoS}_2$, using ZIF-67 as the template *via* multiple hydrothermal and sulfuration process, as shown in Fig. 16d. Fig. 16e shows the TEM image of

$\text{MnO}_2\text{@NiCo-LDH/CoS}_2$. Compared with other electrode in Fig. 16f–i, the $\text{MnO}_2\text{@NiCo-LDH/CoS}_2$ electrode materials have a high specific capacitance of 1547 F g^{-1} at a current density of 1 A g^{-1} and 1189 F g^{-1} at 10 A g^{-1} , exhibiting high rate performance (76.9%) and high stability (82.3%). Also, Zardkhoshoui *et al.*¹³⁵ synthesized nanosheet-assembled hollow $\alpha\text{-MnS@Co}_3\text{S}_4$ spheres (NSH-MCS) with special morphology using ZIF-67 grown on manganese-glycerate (Mn-G) solid spheres as the precursor. The special structure can

provide rich mass/electron transfer channels, and meanwhile prevent the accumulation of nanosheets. Taking advantage of these great merits, the NSH-MCS-based electrode exhibited appealing electrochemical features including an impressive capacity value of 283.3 mA h g⁻¹ (1019.9 C g⁻¹) at 1 A g⁻¹ with the desirable rate performance of 81.5% at 25 A g⁻¹ and significant longevity of 92.7% over 10 000 cycles at 15 A g⁻¹. Also, the hybrid supercapacitor assembled with NSH-MCS as the positive electrode and AC (activated carbon) as the negative electrode exhibited a desirable performance, such as a good energy density (54.9 W h kg⁻¹ at 753 W kg⁻¹) and excellent longevity of 90.5% after 10 000 cycles at 15 A g⁻¹. Additionally, as shown in Fig. 16j, Guan *et al.*¹²³ prepared CoS_x/Ni-Co LDH *via* the partial sulfuration of ZIF-67 and etching and precipitation of the added nickel ions. The prepared CoS_x/Ni-Co LDH nanocages consisted of a hollow rhombic dodecahedral morphology with many nanosheet arrays on their shell. When used as the electrode material for electrochemical capacitors, the CoS_x/Ni-Co LDH nanocages delivered a specific capacitance of 1562 F g⁻¹ at a current density of 1 A g⁻¹. In addition, the asymmetric supercapacitor assembled with CoS_x/Ni-Co LDH as the cathode and activated carbon (AC) as the anode showed a high energy density of 35.8 W h kg⁻¹ at a power density of 800 W kg⁻¹ and an excellent cycling performance with the retention rate of 94.56% after 10 000 cycles, suggesting its potential application in high-performance electrochemical capacitors. These exceptional electrochemical properties can be attributed to the unique structure and synergistic effects between the metal sulfide and the bimetallic hydroxide. Similarly, Wang *et al.*¹⁵⁹ directly grew ZIF-67-derived CoS with Ni(OH)₂ nanosheets on carbon cloth (Ni(OH)₂/CoS/CC) and the composites possessed a superior performance (561.6 mA h g⁻¹ at 1 A g⁻¹) to the Ni(OH)₂/CC electrode (199.4 mA h g⁻¹). The hybrid supercapacitor (HSC) with Ni(OH)₂/CoS/CC as the cathode and activated carbon (AC) as

the anode (Ni(OH)₂/CoS/CC//AC) provided a remarkable energy density of 90.8 W h kg⁻¹ at 800 W kg⁻¹ and maintained 59.7 W h kg⁻¹ even at 25 600 W kg⁻¹, which is higher than that of most of the reported Ni(OH)₂-related devices, and possessed a marvelous capacity retention of 92.2% over 10 000 charge-discharge cycles. The outstanding electrochemical performance of Ni(OH)₂/CoS/CC was chiefly due to the mediation of the Co²⁺/Co³⁺ redox cycle for the rapid conversion of Ni²⁺ into Ni³⁺, which greatly boosted the charge-transfer efficiency in the supercapacitor and methanol electro-oxidation. Moreover, Xue *et al.*¹⁵² used one-dimensional (1D) V₂O₅ nanowires as a flexible backbone to string ZIF-67-derived hollow Co₃S₄ three-dimensional (3D) nanopholyhedra to build robust core-shell 1D@3D V₂O₅@Co₃S₄ nanocomposites (Fig. 16k). As shown in Fig. 16l and m, the 1D V₂O₅ nanowires facilitated efficient electron transportation between the Co₃S₄ nanopolyhedra. The hollow/porous structure of Co₃S₄ not only afforded substantial electroactive sites, but also shortened the charge transport pathway. With these advantages, the optimal V₂O₅@Co₃S₄-5 h displayed enhanced electrochemical properties compared with the control V₂O₅ or Co₃S₄-5 h in a three-electrode system, as shown in Fig. 16n. Furthermore, the asymmetric supercapacitor made from V₂O₅@Co₃S₄-5 h exhibited a high energy density (40.7 W h kg⁻¹ at 800 W kg⁻¹) with outstanding cycle durability, maintaining 85.9% of its initial capacitance after 10 000 cycles.

4. ZIF-67-derived transition metal selenides

Similar to sulfides, ZIF-67-derived transition metal selenides also have the advantages of improved redox-active sites, high specific capacity, better electronic conductivity and thermal and mechanical stability (as shown in Table 3). Additionally,

Table 3 Summary of the electrochemical characteristics of ZIF-67-derived selenide materials in three-electrode measurements

Electrode materials	Specific capacity	Electrolyte	Potential window (CV)	Capacity retention	Cyclic stability	Ref.
Co-Zn-Se@CNTs-CNFs	1891 F g ⁻¹ at 1 A g ⁻¹	6 M KOH	0–0.7 V (Hg/HgO)	52.4% (1 to 30 A g ⁻¹)	97.2% (5000)	184
H-Ni-Co-Se	1175 F g ⁻¹ at 1 A g ⁻¹	6 M KOH	–0.2–0.6 V (SCE)	72.8% (1 to 10 A g ⁻¹)	89.3% (2000)	185
NiSe ₂ /CoSe ₂	1668 F g ⁻¹ at 1 A g ⁻¹	3 M KOH	0–0.7 V (Hg/HgO)	82.8% (1 to 20 A g ⁻¹)	87.2% (5000)	186
P-(Ni, Co)Se ₂	755 C g ⁻¹ at 2 mA cm ⁻²	3 M KOH	0–0.6 V (Hg/HgO)	86.4% (2 to 30 mA cm ⁻²)	80.1% (3000)	187
Ni _{1-x} Co _{1-x} Se ₂ /CNFs/CoO@CC	207.8 mA h g ⁻¹ at 1 A g ⁻¹	6 M KOH	0–0.5 V (Hg/HgO)		104.1% (5000)	188
CoSe ₂ /GO	108.31 mA h g ⁻¹ at 1 A g ⁻¹	2 M KOH	–0.2–0.6 V (SCE)	61.6% (1 to 10 A g ⁻¹)	91.2% (5000)	189
CoSe ₂ /C	462 F g ⁻¹ at 5 A g ⁻¹	2 M KOH	0–0.8 V (SCE)	63.3% (1 to 10 A g ⁻¹)	100% (10 000)	190
NiCoSe ₂ /C	232.6 mA h g ⁻¹ at 1 A g ⁻¹	2 M KOH	0–0.5 V (SCE)	72.6% (1 to 10 A g ⁻¹)	88.3% (5000)	191
CMS-DSHNCs	1029.8 C g ⁻¹ at 2 A g ⁻¹	3 M KOH	–0.3–0.7 V (Ag/AgCl)	76.14% (2 to 50 A g ⁻¹)	95.2% (8000)	192
CoNiSe ₂ /Fe-CoNiSe ₂	1091.2 C g ⁻¹ at 1 A g ⁻¹	3 M KOH	0–0.5 V (Ag/AgCl)	55% (1 to 20 A g ⁻¹)	85% (5000)	193
MXene@CoSe ₂ /Ni ₃ Se ₄	283 mA h g ⁻¹ at 1 A g ⁻¹	3 M KOH	0–0.5 V (Hg/HgO)	62% (1 to 10 A g ⁻¹)	80% (5000)	194
H-NiCoSe ₂ /NC	1131 C g ⁻¹ at 1 A g ⁻¹	3 M KOH	–0.1–0.8 V (Ag/AgCl)	59.2% (1 to 10 A g ⁻¹)	90.2% (6000)	195
CoSe ₂	269.4 mA h g ⁻¹ at 1 A g ⁻¹	6 M KOH	0–0.5 V (Hg/HgO)	83.7% (1 to 20 A g ⁻¹)	83.4% (5000)	196
CoSe ₂ /NC	554.4 F g ⁻¹ at 1 A g ⁻¹	2 M KOH	0–0.8 V (Hg/HgO)	78% (1 to 10 A g ⁻¹)	92% (21 000)	197
CoSe/NC	746 F g ⁻¹ at 2 mV s ⁻¹	3 M KOH	0–0.5 V (Ag/AgCl)	9.5% (2 to 50 mV s ⁻¹)	82.3% (4000)	198
M-(Ni, Co)-Se@CNFs/CC	378.9 mA h g ⁻¹ at 1 A g ⁻¹	6 M KOH	0–0.5 V (Hg/HgO)	72.8% (1 to 10 A g ⁻¹)		199
CoSe ₂ @NiMn-LDH@Cu _{1.6} Se	7064 mF cm ⁻² at 2 mA cm ⁻²	6 M KOH	0–0.5 V (Hg/HgO)		80.11% (10 000)	200
CFP/PNCNF(Se ₁₀)/PEDOT@300	378.1 F g ⁻¹ at 1 A g ⁻¹	1 M H ₂ SO ₄	0–0.7 V (Ag/AgCl)	19% (1 to 32 A g ⁻¹)		33
60-MoSe ₂ /(Ni,Co)Se ₂	359.9 mA h g ⁻¹ at 1 A g ⁻¹	6 M KOH	0–0.6 V (Hg/HgO)	82.3% (1 to 10 A g ⁻¹)	83.7% (10 000)	201
NiSe/Ni ₃ Se ₂ /CoSe/MoSe ₂	15.49 F cm ⁻² at 5 mA cm ⁻²	6 M KOH	–0.2–0.8 V	55.1% (5 to 50 mA cm ⁻²)	96.5% (10 000)	202

as a type of nucleophile, Se not only has a faster reaction speed with active oxygen but also is easier to be restored than the S–O bond due to the existence of a π bond in the Se–O bond, which effectively avoids the occurrence of permanent oxidation and improves the cycling stability of selenides.³⁴ Therefore, ZIF-67-derived transition metal selenides have attracted increasing attention in supercapacitor application.

4.1 Single metal selenides

Shaikat *et al.*¹⁹⁸ synthesized CoSe/NC based on ZIF-67 as the precursor and varying amounts of selenium powder by high-temperature treatment. Compared with the other electrodes with different amounts of Se, CoSe-1 (ZIF-67:Se 1:1) showed an excellent electrochemical performance with the highest specific capacitance (746 F g^{-1} at 2 mV s^{-1}), showing a cyclic capability of 82.3% after 4000 cycles because of the optimized ratio of cobalt and selenium in it. At the same time, Wang *et al.*¹⁹⁷ obtained CoSe₂/NC *via* a similar strategy at various temperatures. In a three-electrode system with 2 M KOH as the electrolyte, CoSe₂/NC-1 h possessed a high capacity of 554.4 F g^{-1} at 1 A g^{-1} and excellent cycling stability (92% capacity retention after 21 000 cycles). In addition, a flexible solid-state supercapacitor was assembled with CoSe₂/NC-1 h as the positive electrode and AC as the negative electrode. The power density was 800 W kg^{-1} at 1 A g^{-1} , and the cycling stability was tested at 91.53% after 6000 cycles at 2 A g^{-1} . Additionally,

Wei's group¹⁹⁰ grew CoSe₂ on carbon cloth using leaf-like ZIF-67 as the precursor by a two-step calcination method (Fig. 17a–c). The novel CoSe₂/carbon (CoSe₂/C) electrode showed an excellent electrochemical performance (Fig. 17d and e), with a specific capacitance of 462 F g^{-1} at a current density of 5 A g^{-1} , and 100% capacitance retention at 10 A g^{-1} after 10 000 cycles. Meanwhile, an asymmetric supercapacitor was assembled, which exhibited an energy density of 20.6 W h kg^{-1} with a power density of 698.8 W kg^{-1} and outstanding cycling stability. Moreover, Fan *et al.*¹⁹⁶ prepared porous CoSe₂ nanosheets on nickel foam *via* the hydrothermal method (Fig. 17f and g). The unique nanosheet array structure could provide a highly active surface, large superficial area and fast ion transport channels. This was mainly attributed to the fact that the reaction at different hydrothermal temperatures can provide different nanosheet structures. In addition, the incorporated ZIF-67 backbone provided a pathway for rapid electron transfer and accommodated the volume expansion of the selenide during charge–discharge processes. As shown in Fig. 17h–k, due to its distinct porous structure, the CoSe₂-180 electrode showed a high specific capacity of $269.4 \text{ mA h g}^{-1}$ at 1 A g^{-1} and a distinguished retention rate of 83.7% at 20 A g^{-1} . After 5000 cycles, the specific capacity was maintained at 83.4% of the initial value. Moreover, the asymmetric supercapacitor (ASC) device was assembled with CoSe₂-180 as the positive electrode. It displayed a favorable electrochemical per-

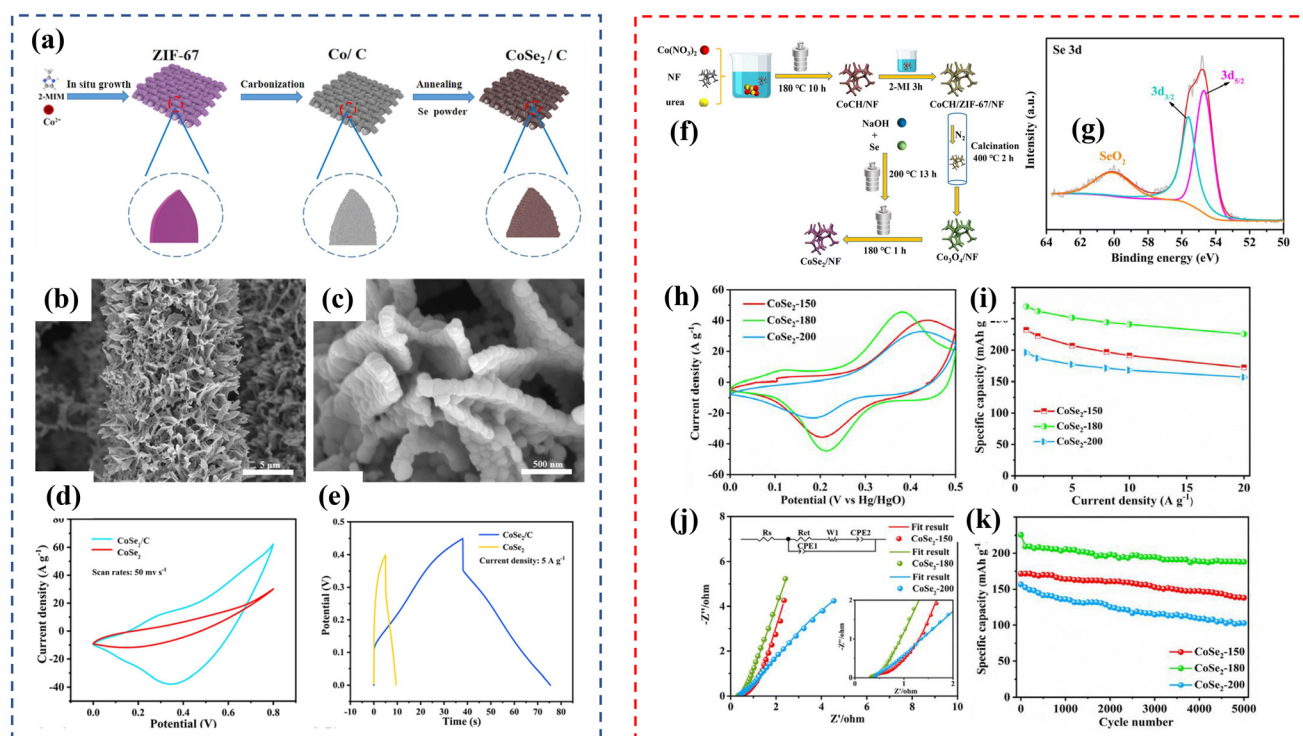


Fig. 17 (a) Schematic of the CoSe₂/C lamellar array; (b and c) SEM images of CoSe₂/C; (d) CV curves at 50 mV s^{-1} and (e) GCD curves at 5 A g^{-1} of CoSe₂ and CoSe₂/C. Reprinted with permission from ref. 190, Copyright 2021, Elsevier B.V. (f) Schematic of the CoSe₂ electrode preparation process; (g) high-resolution XPS patterns of Se 3d; (h) CV curves at 10 mV s^{-1} , (i) specific capacitance, (j) Nyquist plots and (k) cycling performance of CoSe₂-T electrode. Reprinted with permission from ref. 196, Copyright 2023, The Royal Society of Chemistry.

formance with the maximum specific energy of 45.6 W h kg⁻¹ at a specific power of 800.8 W kg⁻¹ and original capacitance retention rate of 81.5% after 5000 cycles.

4.2 Multi-metal selenides

Also, Tan *et al.*¹⁸⁵ successfully assembled nickel cobalt selenide (H-Ni-Co-Se) nanoarrays with a hollow structure from pentagon-like Ni/Co-ZIF on Ni foam by employing a sequential chemical etching and selenylation strategy. The hollow configuration grown on Ni-foam could offer a rich electroactive region, shorten the charge/ion diffusion length and enhance the mass/electrons transfer. Consequently, the as-prepared H-Ni-Co-Se delivered a favorable specific capacitance of 1175 F g⁻¹ at 1 A g⁻¹, fast charge/discharge rate and excellent long-term stability. Similarly, Wang *et al.*¹⁹¹ reported the preparation of a hollow NiCoSe₂/C through a step-by-step derivatization method as a high-performance supercapacitor electrode. Hollow nickel-cobalt bimetallic layered hydroxide (NiCo-LDH) derived from ZIF-67 was selenized to NiCoSe₂ *via in situ* selenylation, which was then coated with a layer of carbon *via* the hydrothermal method using glucose as the carbon source. The electrochemical performances of the as-synthesized NiCoSe₂/C were investigated, and the results indicated that the hollow NiCoSe₂/C exhibited a considerable specific capacity of 232.6 mA h g⁻¹ at 1 A g⁻¹, good rate capability of 72.6% and high capacity retention of 88.3% after 5000 cycles. Compared with ZIF-67, NiCo-LDH and NiCoSe₂, the greatly enhanced electrochemical performances of NiCoSe₂/C can be attributed to the hollow nanostructure of NiCoSe₂, enhanced electrical conductivity by the introduction of Se and C, and inhibited volume changes during the redox cycling from the protection of the carbon layer. Salehan *et al.*¹⁹⁵ also synthesized a cobalt-nickel selenide nitrogen-doped carbon (H-CoNiSe₂/NC) hollow polyhedral composite structure and the presence of the NC structure in the proposed composite could simultaneously lead to improved conductivity and reduce the volume effect created during the cycling procedure. The H-CoNiSe₂/NC electrode provided a high specific capacity (1131 C g⁻¹ at 1.0 A g⁻¹) and outstanding cyclic stability (90.2% retention after 6000 cycles). In addition, the H-CoNiSe₂/NC//AC hybrid supercapacitor delivered an ultrahigh energy density and power density (81.9 W h kg⁻¹ at 900 W kg⁻¹, respectively) and excellent cyclic stability (92.1% of the initial capacitance after 6000 cycles). Additionally, Zong *et al.*¹⁸⁷ successfully designed and fabricated P-(Ni, Co)Se₂ nanoarrays on activated carbon cloth with PBA nanocubes anchored on nanoflakes-nanowires *via* a facile hydrothermal method, followed precipitate reaction and phosphorization/selenylation treatment (Fig. 18a). The continuous hollow PBA nanocubes and appropriate incorporation of P in (Ni, Co)Se₂ could greatly increase the active surface area and enhance the ion diffusion and charge transfer. The reaction is shown as the following equations:



The resultant P-(Ni, Co)Se₂ NA electrode delivered a high areal capacity of 3.02 C cm⁻² (a specific capacity of 755 C g⁻¹) at 2 mA cm⁻² and a good rate capability (2.61 C cm⁻² at 30 mA cm⁻²), as shown in Fig. 18b–e. Furthermore, an all-solid-state hybrid supercapacitor device was also constructed using P-(Ni, Co)Se₂ NAs and ZIF-8-derived carbon as the positive electrode and negative electrode, respectively, which showed a high energy density of 45.0 W h kg⁻¹ at the power density of 446.3 W kg⁻¹. Moreover, Andikaey *et al.*¹⁹³ developed trimetallic CoNiSe₂/Fe-CoNiSe₂ yolk-shell nanoboxes (YSBs) using ZIF-67/NiCoFe Prussian blue analogue (PBA) precursors. Structural engineering of the PBA framework with Co-Fe oxide increased the topological complexity of the nanostructure. The energy storage activity was effectively improved because of the open structure and larger surface area. The presence of trimetallic selenides in CoNiSe₂/Fe-CoNiSe₂ YSBs improved the electronic structures, and thus the electrochemical performances, and enhanced conductivity of the nanostructure compared with its oxide counterparts. As a result, it exhibited an attractive electrochemical performance when used as an electrode for battery-type supercapacitors. CoNiSe₂/Fe-CoNiSe₂ yolk-shell nanoboxes showed a high specific capacity of 1091.2 C g⁻¹ at 1 A g⁻¹, good acceleration performance (55% at 20 A g⁻¹), and excellent cycle stability (85% recovery after 5000 charge-discharge cycles). Furthermore, the CoNiSe₂/Fe-CoNiSe₂ YSB//AC hybrid SC demonstrated an energy density above 76.5 W h kg⁻¹ at a power density of 2378.7 W kg⁻¹.

4.3 Composite materials

Furthermore, Lv *et al.*¹⁸⁴ reported the preparation of hierarchical “tube-on-fiber” nanostructures composed of carbon nanotubes (CNTs) on carbon nanofibers (CNFs) and impregnated with mixed-metal selenide nanoparticles (Co-Zn-Se@CNTs-CNFs) as high-performance supercapacitors. Co-Zn hybrid zeolitic imidazolate framework-67 (Co-Zn ZIF-67) was electrospun with polyacrylonitrile (PAN) to form nanofibers, which were sequentially thermally treated and subjected to selenylation. The “tube-on-fiber” structure was designed to confine the Co-Zn mixed-metal selenide nanoparticles and prevented their agglomeration. Extruded CNTs rooted in carbon nanofibers further improved the electronic conductivity. The mixed-metal selenide allowed more accommodation space and faradaic reactions compared to the single metal selenide. Based on these merits, the hierarchical Co-Zn-Se@CNTs-CNFs exhibited a high specific capacity of 1040.1 C g⁻¹ (1891 F g⁻¹) at 1 A g⁻¹ with an impressive rate performance in supercapacitors. Furthermore, a hybrid supercapacitor was fabricated with Co-Zn-Se@CNTs-CNFs as the cathode and porous carbon nanofibers as the anode (denoted as Co-Zn-Se@CNTs-CNFs//PCNFs). It delivered a superior energy and power density of 61.4 W h kg⁻¹ and 754.4 W kg⁻¹, respectively, and meanwhile retained an energy density of 31.7 W h kg⁻¹ with the working power of 15 421.6 W kg⁻¹. In addition, the assembled supercapacitor device displayed an excellent capacity retention of 88.6% after 8000 cycles at 5 A g⁻¹. Also, Wang *et al.*¹⁸⁹ reported the facile syn-

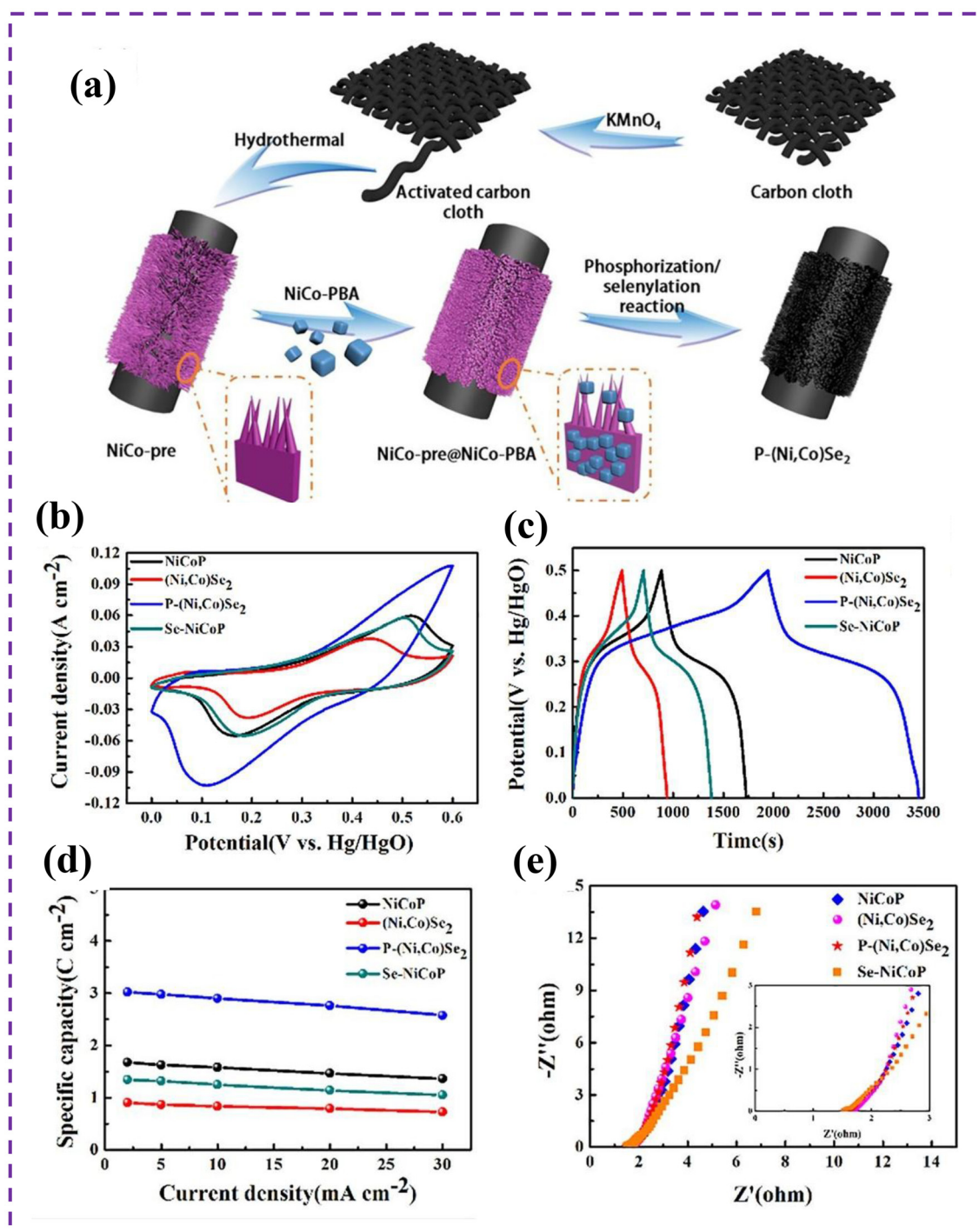


Fig. 18 (a) Schematic of the procedure for the fabrication of P-(Ni, Co)Se₂ NAs on activated carbon cloth; (b) CV curves at 10 mV s⁻¹, (c) GCD curves at 2 mA cm⁻², (d) specific capacitance and (e) Nyquist plots of NiCoP, (Ni, Co)Se₂, P-(Ni, Co)Se₂ and Se-NiCoP. Reprinted with permission from ref. 187, Copyright 2019, Elsevier B.V.

thesis of graphene oxide (GO)-supported CoSe₂ (CoSe₂/GO) derived from ZIF-67 *via* the hydrothermal method. CoSe₂/GO exhibited a considerable specific capacity (108.31 mA h g⁻¹ at 1 A g⁻¹) and high cyclic stability (capacity retention of 91.2% after 5000 cycles). Compared with GO and CoSe₂ alone, the greatly enhanced electrochemical performances of CoSe₂/GO

can be attributed to the synergistic effect of GO and CoSe₂. Additionally, Yang *et al.*¹⁹⁴ synthesized ZIF-67-derived CoSe₂/Ni₃Se₄ nanosheets anchored vertically on an MXene substrate, which enhanced the overall conductivity. Furthermore, the close combination between the CoSe₂/Ni₃Se₄ nanosheets and MXene nanosheets promoted a faster charge transfer rate

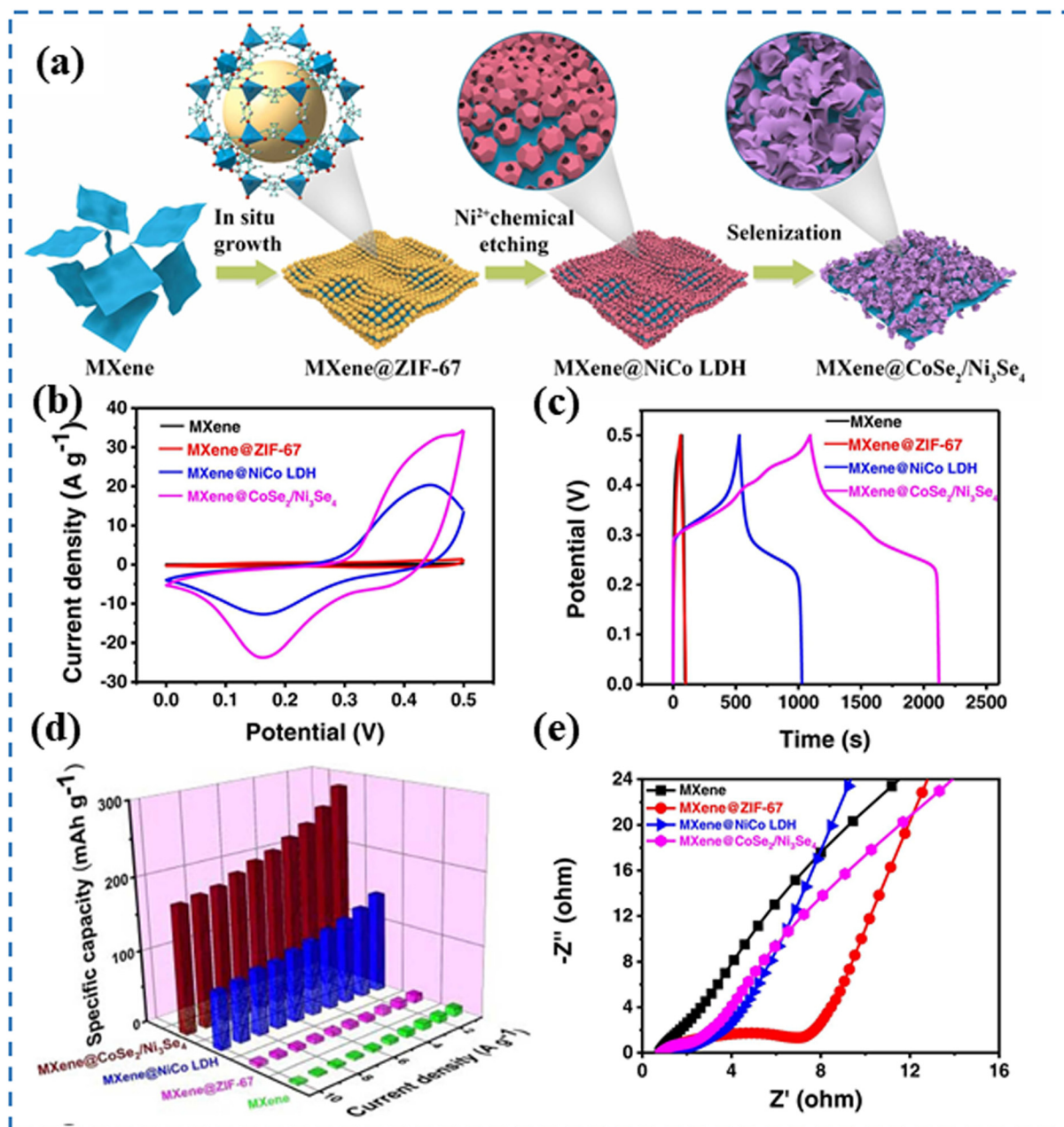


Fig. 19 (a) Schematic of the synthesis of the hierarchical 2D MXene@CoSe₂/Ni₃Se₄ nanosheets and (b) CV curves at 5 mV s⁻¹, (c) GCD curves at 1 A g⁻¹, (d) specific capacitance and (e) Nyquist plots of MXene, MXene@ZIF-67, MXene@NiCo-LDH and MXene@CoSe₂/Ni₃Se₄. Reprinted with permission from ref. 194, Copyright 2022, Elsevier B.V.

and improved the durability of the structure (Fig. 19a). Consequently, as an electrode material for supercapacitors, the honeycomb-like MXene@CoSe₂/Ni₃Se₄ achieved a high specific capacitance (283 mA h g⁻¹ at 1 A g⁻¹, as shown in Fig. 19b–e) and an outstanding capacitance retention rate with 80% after 5000 cycles. Moreover, Shi's group reported the synthesis of M–(Ni, Co)–Se@CNFs/CC¹⁹⁹ and Ni_xCo_{1–x}Se₂/CNFs/CoO@CC¹⁸⁸ derived from ZIF-L for hybrid supercapacitors, respectively. M–(Ni, Co)–Se@CNFs/CC exhibited a specific capacitance of 378.9 mA h g⁻¹ at 1 A g⁻¹, while that

of Ni_xCo_{1–x}Se₂/CNFs/CoO@CC was 207.8 mA h g⁻¹, and both displayed a superior performance and stability.

Meanwhile, Zhang *et al.*²⁰⁰ synthesized a wire-sheet-particle hierarchical hetero-structured CoSe₂@NiMn-layered double hydroxide (NiMn-LDH)@Cu_{1.8}Se/Copper foam (CF) electrode *via* a phase pseudomorphic transformation process achieved by the selective selenization of Cu and Co elements (Fig. 20a). Benefiting from the stable support structure of CuBr₂, the large specific surface area of NiMn-LDH, and the excellent conductivity of CoSe₂, the prepared binder-free electrode showed

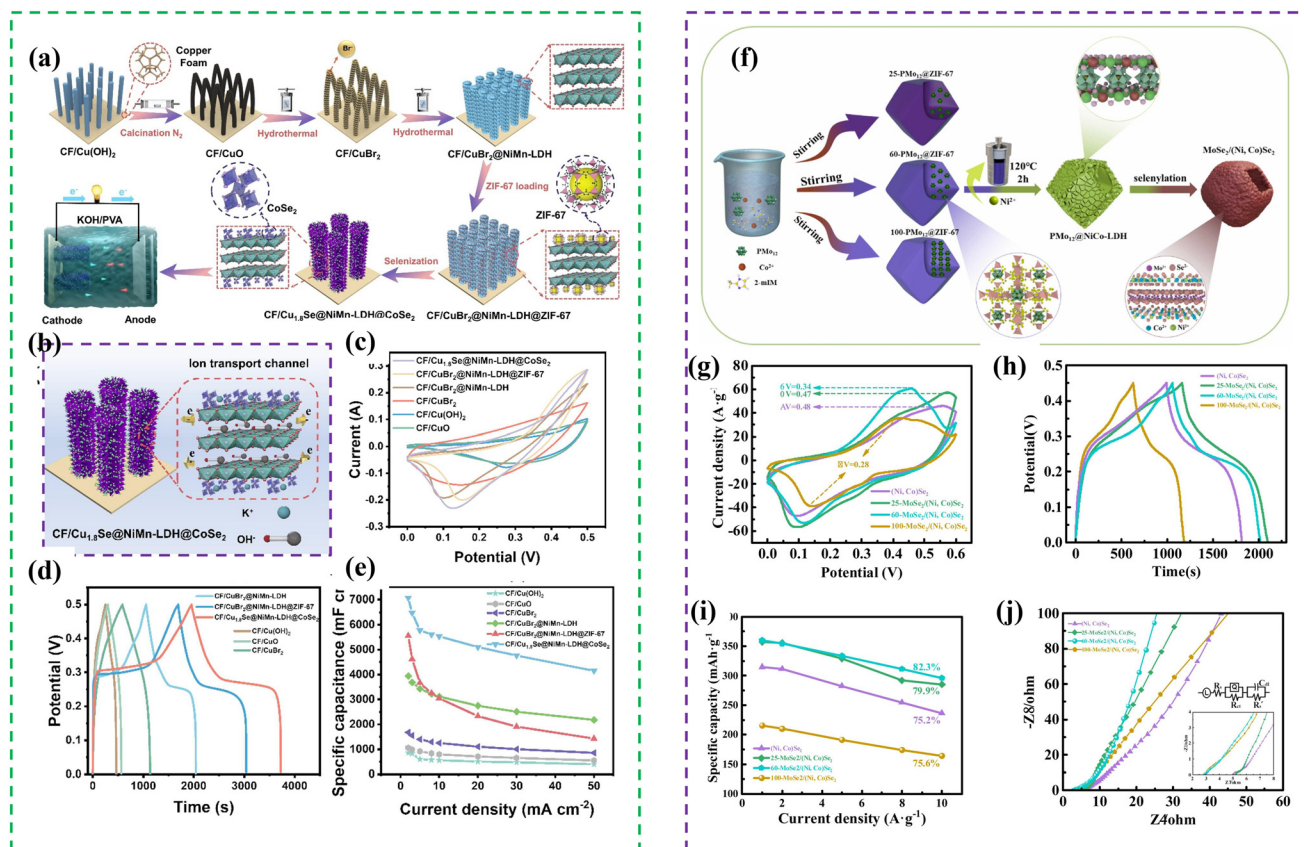


Fig. 20 (a) Schematic depiction of the stepwise formation process of $\text{CoSe}_2\text{@NiMn-LDH@Cu}_{1.8}\text{Se/CF}$ nanosheet arrays derived from ZIF-67-covered CuBr_2 nanorod arrays via selective phase pseudomorphic transformation; (b) schematic of capacitance process of $\text{CoSe}_2\text{@NiMn-LDH@Cu}_{1.8}\text{Se/CF}$; and (c) CV curves, (d) GCD curves and (e) specific capacitance of $\text{CoSe}_2\text{@NiMn-LDH@Cu}_{1.8}\text{Se/CF}$, ZIF-67@NiMn-LDH@ $\text{CuBr}_2\text{/CF}$, NiMn-LDH@ $\text{CuBr}_2\text{/CF}$, $\text{CuBr}_2\text{/CF}$, $\text{Cu(OH)}_2\text{/CF}$ and CuO/CF . Reprinted with permission from ref. 200, Copyright 2023, Elsevier Inc. (f) Schematic illustration of procedure for the preparation of $\text{MoSe}_2\text{/(Ni, Co)Se}_2$ hollow nanomaterials; and (g) CV curves at 15 mV s^{-1} , (h) GCD curves at 1 A g^{-1} , (i) specific capacitance and (j) Nyquist plots of (Ni, Co) Se_2 , 25-Mo $\text{Se}_2\text{/(Ni, Co)Se}_2$, 60-Mo $\text{Se}_2\text{/(Ni, Co)Se}_2$ and 100-Mo $\text{Se}_2\text{/(Ni, Co)Se}_2$. Reprinted with permission from ref. 201, Copyright 2024, Elsevier B.V.

excellent electrochemical properties. The $\text{CoSe}_2\text{@NiMn-LDH@Cu}_{1.8}\text{Se}$ hybrid electrode exhibited a superior specific areal capacitance of 7064 mF cm^{-2} at 2 mA cm^{-2} and a stable cyclic performance with 80.11% capacitance retention after 10 000 cycles (Fig. 20b–e). Furthermore, the assembled $\text{CoSe}_2\text{@NiMn-LDH@Cu}_{1.8}\text{Se/CF//AC}$ (activated carbon) asymmetric supercapacitor (ASC) achieved an energy density of 36.6 W h kg^{-1} at the power density of 760.6 W kg^{-1} and retained 87.35% of its initial capacitance after 5000 cycles. Also, Guo *et al.*²⁰¹ synthesized $\text{MoSe}_2\text{/(Ni, Co)Se}_2$ hollow structures derived from $\text{PMo}_{12}\text{/ZIF-67}$ precursor by an Ni^{2+} etching and selenization process (Fig. 20f). In the three-electrode test, as shown in Fig. 20g–j, the developed 60-Mo $\text{Se}_2\text{/(Ni, Co)Se}_2$ electrode material exhibited an excellent specific capacity of $359.9 \text{ mA h g}^{-1}$ at a current density of 1 A g^{-1} , and a capacitance retention rate of 83.7% after 10 000 cycles. In addition, the asymmetric supercapacitor (ASC) assembled with 60-Mo $\text{Se}_2\text{/(Ni, Co)Se}_2$ as the positive electrode and activated carbon as the negative electrode exhibited an excellent energy density of 40.3 W h kg^{-1} at a power density of 800.9 W kg^{-1} .

5. ZIF-67-derived transition metal tellurides

Similar to sulfides and selenides, tellurides are a newly explored class of chalcogenides in supercapacitors, which exhibit improved metallic properties, larger lattice parameters and higher degree of covalency in anion–metal bonding than sulfides and selenides.²⁰³ Therefore, ZIF-67-derived transition metal tellurides are also new materials worth exploring.

Kshetri *et al.*²⁰⁴ reported the fabrication of a ZIF-67-derived CoTe–carbon porous-structured composite on nickel foam (CoTe@C–NiF) by high-temperature treatment (Fig. 21a). As shown in Fig. 21b–e, in the negative potential regions, the CoTe@C–NiF hybrid electrode exhibited a maximum areal capacitance of 307.5 mF cm^{-2} at a current density of 1 mA cm^{-2} and retained 162.0 mF cm^{-2} at a high current density of 20 mA cm^{-2} , resulting in a rate capability of 52.03%. However, in the positive potential region, the same electrode showed

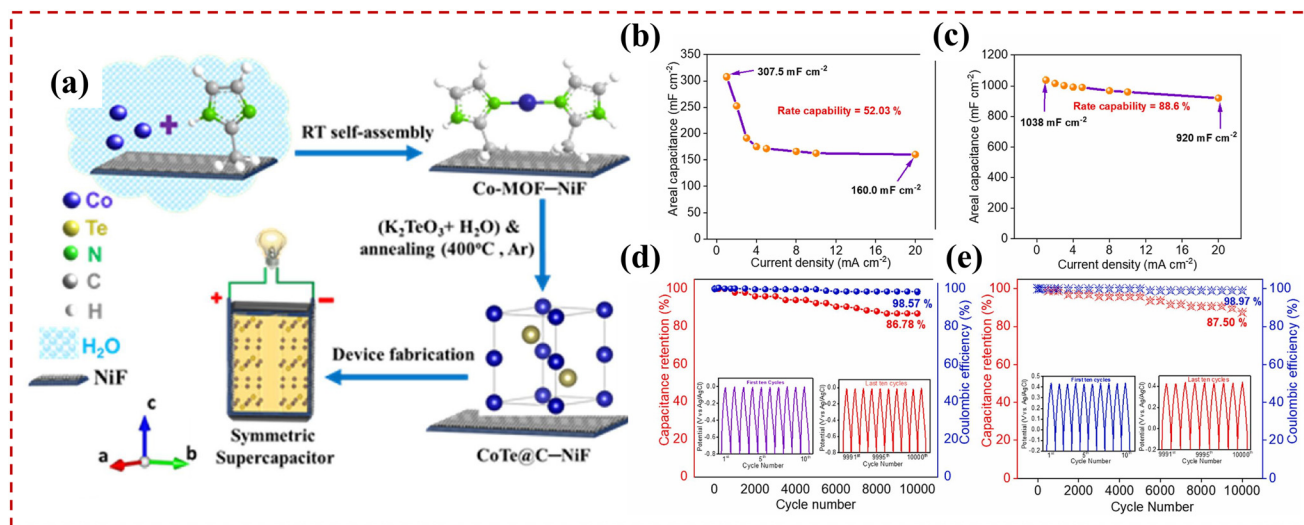


Fig. 21 (a) Schematic for the synthesis of CoTe@C-NiF hybrid electrode; and (b and c) specific capacitance and (d and e) cycling stability of CoTe@C-NiF in the negative and positive potential window, respectively. Reprinted with permission from ref. 204, Copyright 2021, Elsevier Ltd.

areal capacitances of 1038 mF cm⁻² and 920 mF cm⁻², respectively, at the same current densities, resulting in a rate capability of 88.63%. In addition, CoTe@C-NiF showed long-term electrochemical stability during the charge-discharge process in both the negative and positive potential window. In the negative potential window, it showed 86.78% and 98.57% retention of areal capacitance and coulombic efficiency, respectively. Similarly, in the positive window, 87.50% and 98.97% retention of areal capacitance and coulombic efficiency was observed after 10 000 charge-discharge cycles, respectively.

6. Summary and perspectives

6.1 Summary

Supercapacitors (SCs) are generally regarded as promising electrochemical devices in the field of energy storage due to their advantages of fast charge-discharge rate and long cyclic term. However, the low energy density of SCs limits their further application. In this case, electrode materials, as one of the components of SCs, play an important role in the electrochemical performance of energy storage devices. Thus, to improve the energy density of SC devices, it is essential to look for or synthesize new electrode materials. Recently, ZIF-67 has attracted considerable attention as an electrode material for SC application because of its controllable pore rate, constant cavity and large specific area. Also, pristine ZIF-67 and ZIF-67 derivatives such as porous carbon, metal-doped carbon, hydroxides (Table S3†), phosphides (Table S4†) and chalcogenides (including oxides, sulfides, selenides and tellurides) have shown exemplary performances in supercapacitors but still have some challenges that need to be overcome. Therefore, in this review, we discussed ZIF-67-derived chalcogenides as electrode materials for SCs

including their preparation strategies, micro structure and electrochemical properties. Generally, as a typical pseudocapacitor materials, ZIF-67-derived chalcogenides have a larger specific capacitance and higher energy density than pristine ZIF-67 and ZIF-67-derived carbon materials. However, that still have some disadvantages such as the slightly lower capacity for oxides with high structural stability and volume expansion and structural destruction during long-term cycling for sulfides, selenides and tellurides. Therefore, researchers have developed many strategies to solve these questions. For instance, from single metal compounds to multi-metal compounds, the specific capacitance of chalcogenides can be improved greatly due to the changes in their chemical properties. Also, doping metal ions can provide more active sites for electrochemical reactions. Additionally, combining chalcogenides with other materials such as carbon materials (carbon nanotubes and graphene), conductive polymers (PPy, PANI, and PEDOT), 2D MXenes and other transition metal compounds is also an effective way to improve their conductivity and structural stability. Many of the studies mentioned herein have proven the feasibility of these methods.

6.2 Perspectives

ZIF-67 is desirable for a wide range of applications owing to its tailorable surface area, porosity, precise pore size and composition control as key considerations. However, the weak inherent conductivity and structural instability of pristine ZIF-67 restricts its usage in electrochemical applications. ZIF-67-derived chalcogenides have emerged as viable materials for supercapacitor applications due to the strong control of their morphology, functionalization, doping of heteroatoms, enhanced surface area and structural modification. However, there is still many aspects of ZIF-67-derived chalcogenides for SC application worth researching.

- ZIF-67-derived tellurides exhibit excellent electrochemical properties because of their improved metallic properties, large lattice parameters and high degree of covalency in anion-metal bonding. However, there are still few studies about ZIF-67-derived transition metal tellurides. Therefore, more work on tellurides needs further research in the future.

- There are still certain shortcomings in the current common preparation methods, as follows: (1) the coprecipitation method is the simultaneous precipitation of soluble and micro-components from the same solution by adsorption, encapsulation or mechanical trapping to form mixed crystals. However, ZIF-67 prepared by this method has poor uniformity unless premium solvents and surfactant are used. (2) The hydrothermal/solvothermal method is a synthesis process in which chemical reagents and solvents are heated inside a high-pressure steel vessel, but has lower yields. (3) Annealing/carbonization is a high-temperature procedure that requires a strict atmosphere and sometimes destroys the structure of ZIF-67. Therefore, it is imperative to improve existing methods and adopt new methods. Surfactants are essential for the coprecipitation method; optimization of the parameters for the hydrothermal/solvothermal and annealing/carbonization methods, such as time, temperature and atmosphere, should be evaluated; and microwave/ultrasonic wave-assisted techniques have become increasingly popular because they cause atoms and molecules to oscillate, effectively initiating chemical processes. Moreover, the electrochemical method is also a good synthesis process due to its quicker synthesis conditions and greater control. Hence, there is a need to evaluate the synthesis of ZIF-67 and its derivatives.

- ZIF-67-derived chalcogenides have a complex composition, including local crystal/amorphous inorganic compounds and organic frameworks/carbon, which increases the difficulty of characterizing the microstructure of these materials. Thus, to further analyze the evolution of substances and structures in material synthesis and electrochemical reactions, organic/inorganic characterization methods should be combined for comprehensive analysis.

- Similarly, due to the complex composition of ZIF-67-derived chalcogenides, they are different from pure chalcogenides in the mechanism of energy storage/conversion systems. Therefore, *in situ* measurements, such as Raman spectroscopy, X-ray diffraction, X-ray absorption spectroscopy, ambient-pressure XPS and electrochemical mass spectrometry, may be useful. Meanwhile, in the process of theoretical calculation, compared to pure chalcogenides, the construction of the model must also consider the existence of frameworks, which may increase the complexity of the work.

- Flexible and wearable micro-supercapacitors and micro-batteries based on ZIF-67-derived chalcogenides with controlled properties together with safe, reliable and intelligent electronic properties also need to be further investigated.

Overall, we believe that the further design and synthesis of ZIF-67-derived chalcogenides need to be studied for meeting the requirements of supercapacitor application.

Author contributions

Lidong Jiao: investigation, formal analysis, writing-original draft, and visualization. Mingshu Zhao: conceptualization, methodology, supervision, funding acquisition, and writing-review & editing. Qingyang Zheng: investigation. Qingyi Ren: investigation and validation. Zhou Su: validation. Min Li: investigation. Feng Li: formal analysis.

Data availability

No primary research results, software or code has been included and no new data were generated or analysed as part of this review.

Conflicts of interest

There are no conflicts to declare.

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