



SPECIAL ISSUE: Innovative Electrode Materials for Supercapacitors

# Hierarchically nanostructured transition metal oxides for supercapacitors

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**ABSTRACT** Highly efficient, clean, and sustainable electrochemical energy storage technologies have been investigated extensively to counter the shortage of fossil fuels and increasingly prominent environmental problems. Supercapacitors (SCs) have received wide attention as critical devices for electrochemical energy storage because of their rapid charging–discharging capability and long life cycle. Various transition metal oxides (TMOs), such as  $\text{MnO}_2$ , NiO,  $\text{Co}_3\text{O}_4$ , and CuO, have been extensively studied as electrode materials for SCs. Compared with carbon and conducting polymers, TMO materials can achieve higher specific capacitance. For further improvement of electrochemical performance, hierarchically nanostructured TMO materials have become a hot research area for electrode materials in SCs. The hierarchical nanostructure can not only offer abundant accessible electroactive sites for redox reactions but also shorten the ion diffusion pathway. In this review, we provide an overall summary and evaluation of the recent progress of hierarchically nanostructured TMOs for SCs, including synthesis methods, compositions, structures, and electrochemical performances. Both single-phase TMOs and the composites based on TMOs are summarized. Furthermore, we also prospect the developing foreground of this field. In this view, the important directions mainly include: the nanocomposites of TMOs materials with conductive materials; the cobalt-based materials and the nickel-based materials; the improvement of the volume energy density, the asymmetric SCs, and the flexible all-solid-state SCs.

**Keywords:** hierarchical nanostructure, transition metal oxides, supercapacitors

## INTRODUCTION

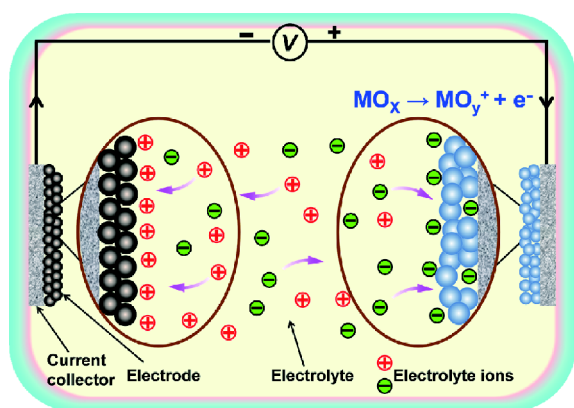
With the rapid development of global economy, energy

shortage and environmental pollution have become two extremely important issues worldwide. A breakthrough in exploiting highly efficient and clean energy storage technologies is necessary to satisfy future energy requirements [1–6]. The electrochemical energy storage is the most promising approach because of its high efficiency, good reliability, ease of operation, and good eco-friendly character [7–18]. Electrochemical energy storage technologies mainly include batteries and supercapacitors (SCs) [19,20]. As a new energy storage approach, SCs combine the advantages of high energy density of rechargeable batteries and high power density of dielectric capacitors [19–29]. SCs have been regarded as highly important candidates for energy storage devices because of their fast charging–discharging capability, long cycle stability ( $>10^5$  cycles), high power density ( $>10 \text{ kW kg}^{-1}$ ), low cost, environment-friendly nature, low maintenance, and safe operation [30–46]. In certain fields, SCs can partly or fully replace traditional batteries.

SCs can be divided into two categories according to energy storage mechanism: electrical double-layer capacitors (EDLCs) (Fig. 1a) and pseudocapacitors (Fig. 1b) [19–21]. The capacitance of EDLCs is associated with the charge separation and accumulation at the interface between electrode and electrolyte [19–21]. During charging, the electric charges on the surface of electrode attract the ions with opposite charges in the electrolyte. Thus, the electric double layer is formed on the surface of electrode and the energy storage is realized. The capacitance stored in the electric double layer is proportional to the specific surface area of the electrode. During discharging, ions return to the electrolyte and electrons flow into the external circuit. Nanostructured carbon materials, such as mesoporous carbon, activated carbon, carbon nanotubes,

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**Figure 1** Schematic of the two different mechanisms of SCs: (a) EDLCs and (b) pseudocapacitors.

carbon nanofibers, and graphene, have been widely studied as the electrode materials of EDLCs. The capacitance of pseudocapacitors is derived from the fast and reversible Faradaic process (redox reactions) occurring on the surface or near surface of the electrode materials [19–21]. Although the generation process of pseudocapacitance involves redox reactions, it is different from the reaction process of battery. The battery is controlled by the ion diffusion within the crystalline framework of active material; while the pseudocapacitor is not limited by the diffusion process [19]. Therefore, the pseudocapacitor possesses highly dynamic reversibility and is more closer to the characteristics of the capacitor. The electrode materials of pseudocapacitors mainly include transition metal oxides (TMOs) and conductive polymers.

Conventional carbon material-based EDLCs usually exhibit low specific capacitance [19,20]. TMOs, which possess multiple oxidation states, could achieve markedly larger specific capacitance than carbon materials [19,20]. Early investigations on electrode materials have concentrated on noble TMOs, such as  $\text{RuO}_2$  and  $\text{IrO}_2$ .  $\text{RuO}_2$  with three oxidation states within 1.4 V, indicating a large specific capacitance of  $2000 \text{ F g}^{-1}$  [47,48]. However, the exceedingly high cost and environmentally poisonous nature limit their practical applications. Hence, cheap and high-performance TMOs, such as  $\text{MnO}_2$ ,  $\text{NiO}$ ,  $\text{Co}_3\text{O}_4$ , and  $\text{CuO}$ , have been extensively studied as the electrode materials for SCs [49–54]. Moreover, multiple-metal TMOs, such as  $\text{NiCo}_2\text{O}_4$ ,  $\text{NiCoO}_2$ , and  $\text{ZnV}_2\text{O}_4$ , have also attracted considerable interest because these materials can provide better electrochemical performance compared with single-metal TMOs [55–57]. TMOs with a variety of structures and morphologies, such as thin films, nanowires/nanorods, nanotubes, nanosheets, nanoflowers, and

hollow nanospheres, have been fabricated *via* different synthesis routes [49–60]. Moreover, their electrochemical properties have been extensively investigated.

Hierarchically nanostructured materials are self-assembly systems that are assembled from low dimensional nanobuilding blocks, such as nanoparticles (NPs), nanowires, nanorods, nanotubes, and nanosheets [61,62]. Recently, hierarchically nanostructured TMO materials have gradually become a research hotspot in SC field because of their unique structures [63–67]. These structures could offer large specific surface area, abundant accessible electroactive sites, and short ion diffusion pathway during the rapid charge–discharge process [63–67]. Hierarchically nanostructured TMOs exhibit higher power properties, larger specific capacitances, and more outstanding cycle stabilities compared with common TMOs. In this review, we mainly expound the topic of hierarchically nanostructured TMO electrode materials for SCs. The synthesis and electrochemical performance of hierarchically nanostructured single- or multiphase TMOs are systematically reviewed. We emphasize on several advanced TMO-based composite materials with excellent electrochemical properties, which mainly originate from advantageous compositional and structural characteristics. In addition, we propose several personal prospects to motivate further development of hierarchically nanostructured TMOs for SCs.

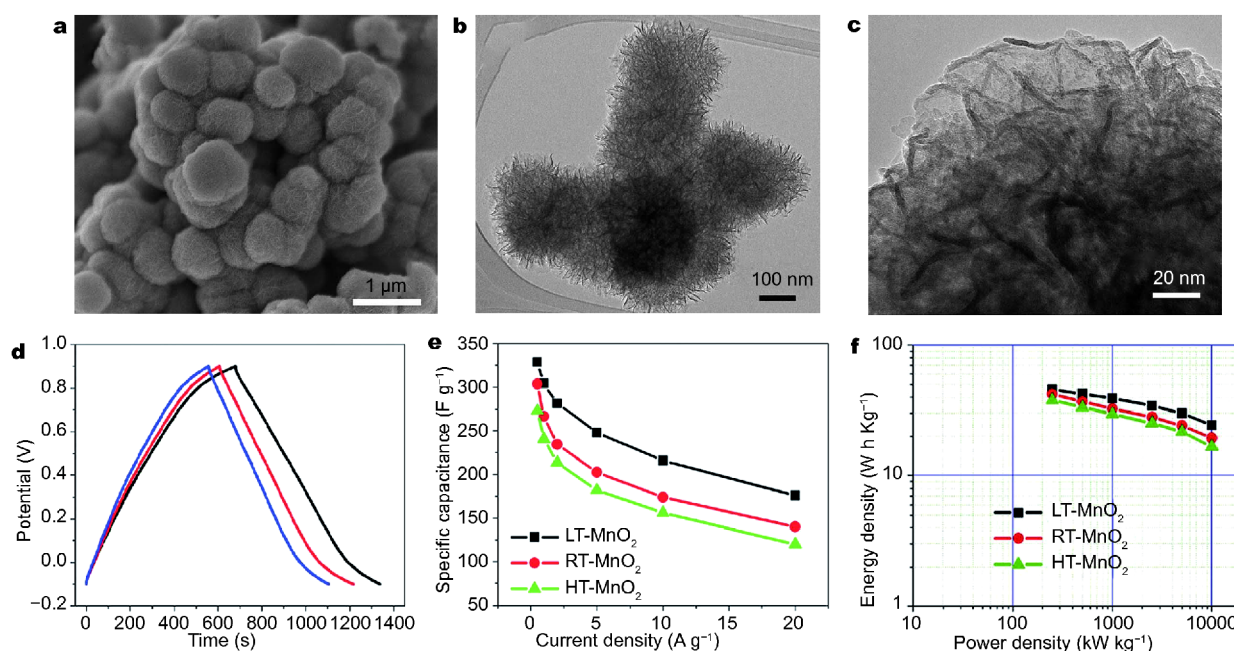
The following sections describe the hierarchically nanostructured TMOs as electrode materials for SCs. The summary mainly is divided into two parts: one is single-phase TMOs, and the other is the composites based on TMOs. Unless otherwise noted, the electrochemical tests are mainly investigated in three-electrode systems. The electrolytes for all works are shown in parentheses.

## HIERARCHICALLY NANOSTRUCTURED SINGLE-PHASE TMOs FOR SCs

### Manganese oxides

Electrochemical SCs based on manganese dioxide ( $\text{MnO}_2$ ) have attracted considerable interest because of its rich polymorphisms ( $\alpha$ -,  $\beta$ -,  $\gamma$ -,  $\delta$ -,  $\lambda$ -, and  $\epsilon$ -type), high theoretical specific capacitance, high natural abundance, and good environmental compatibility [68–75].

Flower-like hierarchical  $\alpha$ - $\text{MnO}_2$  sub-microspheres were successfully fabricated by Yuan and coworkers *via* a novel interfacial strategy [76]. The Brunauer–Emmett–Teller (BET) specific surface area of the  $\alpha$ - $\text{MnO}_2$  sample is  $216 \text{ m}^2 \text{ g}^{-1}$ . To evaluate electrochemical performance, the hierarchical  $\alpha$ - $\text{MnO}_2$  material was investigated *via* cyclic



**Figure 2** (a) SEM and (b), (c) TEM images of the LT-MnO<sub>2</sub>. Electrochemical properties of the three samples; (d) galvanostatic charge–discharge curves at 0.5 A g<sup>-1</sup>; (e) specific capacitances at various current densities; (f) Ragone plots. Reproduced with permission from Ref. [79]. Copyright 2012, the Royal Society of Chemistry.

voltammetry (CV), cyclic chronopotentiometry (CC), and electrochemical impedance spectroscopy in 1 mol L<sup>-1</sup> K<sub>2</sub>SO<sub>4</sub>. The electrochemical measurement results in high specific capacitances of 298 and 236 F g<sup>-1</sup> at 0.117 and 2.353 A g<sup>-1</sup>, respectively. Furthermore, the α-MnO<sub>2</sub> sample shows 90% retention after 2,000 cycles at 2 A g<sup>-1</sup>. The good performance is ascribed to the special hierarchical structure and rich MnO<sub>2</sub>-electrolyte interfaces.

Lee *et al.* [77] prepared hierarchical nanostructures of hydrated α-MnO<sub>2</sub> by one-step synthesis at room temperature. The α-MnO<sub>2</sub> sample consists of small ultrathin nanorod-like structures with diameters of 2–4 nm. The MnO<sub>2</sub> electrode delivers a high specific capacitance of 356 F g<sup>-1</sup> at 2 A g<sup>-1</sup> (1 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub>). After 2,000 cycles of cycling test, no capacitance degradation is observed.

β-MnO<sub>2</sub> as electrode material in SCs is also investigated. Zhao *et al.* [78] successfully fabricated hierarchical porous β-MnO<sub>2</sub> nanoflowers assembled by ultrathin nanoplates at room temperature. The BET specific surface area of the β-MnO<sub>2</sub> sample is as high as 267 m<sup>2</sup> g<sup>-1</sup>. The electrochemical measurements demonstrate that the sample possesses a large energy density of 22.6 W h kg<sup>-1</sup> at a high power density of 9.1 kW g<sup>-1</sup>, with a high specific capacitance of 201.5 F g<sup>-1</sup> (1 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub>). Furthermore, at 2 mV s<sup>-1</sup>, the specific capacitance reaches up to 296.3 F g<sup>-1</sup>, which is evidently superior to

those of β-MnO<sub>2</sub> powders (~7 F g<sup>-1</sup>) and β-MnO<sub>2</sub> nanorods (14.9 F g<sup>-1</sup>).

Using a simple and scalable method, Li *et al.* [79] prepared hierarchical MnO<sub>2</sub> nanostructures assembled by ultrathin nanoflakes. The resulting products labeled as LT-MnO<sub>2</sub>, RT-MnO<sub>2</sub>, and HT-MnO<sub>2</sub> (LT, RT, and HT represent low temperature, room temperature, and high temperature, respectively) were synthesized by conducting the reaction in an ice bath, at room temperature, and at 100 °C. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of LT-MnO<sub>2</sub> are shown in Fig. 2a–c. The MnO<sub>2</sub> nanospheres are assembled by small nanoflakes with low crystallinity. The LT-MnO<sub>2</sub> displays the largest specific surface area (269.0 m<sup>2</sup> g<sup>-1</sup>) compared with the RT-MnO<sub>2</sub> (173.6 m<sup>2</sup> g<sup>-1</sup>) and HT-MnO<sub>2</sub> (164.6 m<sup>2</sup> g<sup>-1</sup>). In addition, the LT-MnO<sub>2</sub> possesses the highest specific capacitance (176 F g<sup>-1</sup>) at 20 A g<sup>-1</sup> (1 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub>) compared with the RT-MnO<sub>2</sub> (140 F g<sup>-1</sup>) and HT-MnO<sub>2</sub> (120 F g<sup>-1</sup>) (shown in Fig. 2d, e). As shown in Fig. 2f, at a power density of 250 W kg<sup>-1</sup>, the LT-MnO<sub>2</sub> also shows the highest energy density of 45.6 W h kg<sup>-1</sup> among the three samples (RT-MnO<sub>2</sub> with 42.2 W h kg<sup>-1</sup> and HT-MnO<sub>2</sub> with 37.9 W h kg<sup>-1</sup>) [76–79].

Raj *et al.* [80] synthesized hierarchical mesoporous δ-MnO<sub>2</sub> via an easy single-step and template-free method.

This hierarchical mesoporous  $\delta$ -MnO<sub>2</sub> has a large BET specific surface area of 238 m<sup>2</sup> g<sup>-1</sup>. The specific capacitance of  $\delta$ -MnO<sub>2</sub> is 364 F g<sup>-1</sup> at 1 A g<sup>-1</sup> (1 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub>). Furthermore, the asymmetric SCs device with a large voltage window of 0–2 V was fabricated by using  $\delta$ -MnO<sub>2</sub> as the cathode and activated carbon as the anode. The device shows a specific capacitance of 86.5 F g<sup>-1</sup> at 1 A g<sup>-1</sup> and a capacitance retention of 100% after 3,000 cycles at 20 A g<sup>-1</sup>. The device exhibits a high energy density of 48.06 W h kg<sup>-1</sup> at a power density of 1.0 kW kg<sup>-1</sup>.

### Cobalt oxides

Among TMOs, Co<sub>3</sub>O<sub>4</sub> is also considered as a highly promising material due to its cost effectiveness, environmental benignancy, and ultrahigh theoretical specific capacitance (3560 F g<sup>-1</sup>) [81–84]. Cobalt oxides with a variety of structures and morphologies, such as NPs [85], nanowires [86], nanorods [87], nanosheets [88], and porous nanostructures [89,90], have been fabricated *via* electrochemical and/or chemical routes, and the corresponding electrochemical performance is under intensive investigation.

A hydrothermal strategy based on a self-assembled monolayer polystyrene sphere template was used by Cao *et al.* [91] for the fabrication of hierarchical porous Co<sub>3</sub>O<sub>4</sub> film. The Co<sub>3</sub>O<sub>4</sub> film is approximately 20 nm thick. The specific capacitances of the Co<sub>3</sub>O<sub>4</sub> films are 352 and 291 F g<sup>-1</sup> at 2 and 40 A g<sup>-1</sup> (2 mol L<sup>-1</sup> KOH), respectively. These specific capacitances are higher than that of the sample obtained without using a template (325 and 217 F g<sup>-1</sup> at 2 and 40 A g<sup>-1</sup>).

Xiao *et al.* [92] prepared three-dimensional (3D) enoki mushroom-like Co<sub>3</sub>O<sub>4</sub> hierarchitectures *via* an easy reflux method. The primary structure of Co<sub>3</sub>O<sub>4</sub> hierarchitectures is the nanowire with a diameter of approximately 3.2  $\mu$ m. Each Co<sub>3</sub>O<sub>4</sub> nanowire is made up of numerous Co<sub>3</sub>O<sub>4</sub> NPs. The Co<sub>3</sub>O<sub>4</sub> material displays a large specific capacitance of 787 F g<sup>-1</sup> at 1 A g<sup>-1</sup> (6 mol L<sup>-1</sup> KOH), and a capacity retention of 94.5% after 1,000 cycles at 10 A g<sup>-1</sup>. The asymmetric SCs device (carbon materials as anode) exhibits an energy density of 23.9 W h kg<sup>-1</sup> at 0.5 A g<sup>-1</sup>, together with a power density of 0.375 kW kg<sup>-1</sup>. The unique 3D enoki mushroom-like hierarchitectures could evidently improve the rate of ion diffusion and the stability of electrodes, which results in considerable electrochemical performances of the Co<sub>3</sub>O<sub>4</sub> material.

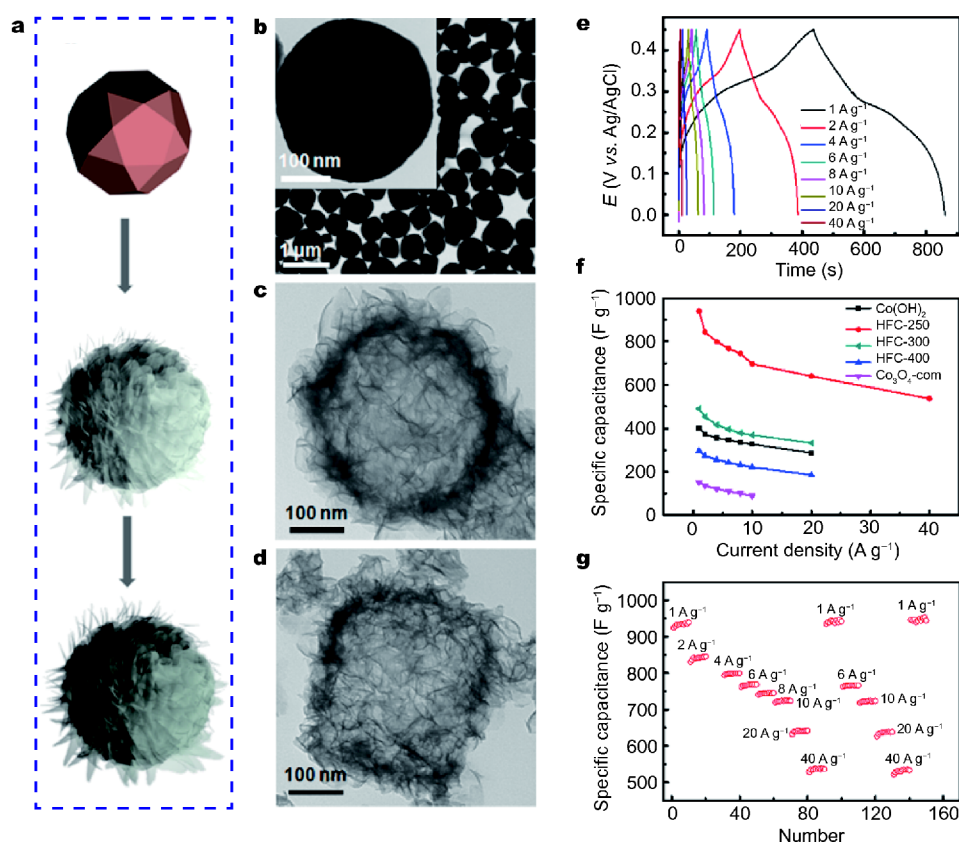
Qu *et al.* [93] reported that hollow fluffy cages (HFC) of Co<sub>3</sub>O<sub>4</sub> were prepared by the formation of Co(OH)<sub>2</sub> hollow cages and subsequent calcination at different

temperature. The HFC of Co<sub>3</sub>O<sub>4</sub> was annealed at 250, 300, and 400°C, respectively. The synthetic scheme for HFC Co<sub>3</sub>O<sub>4</sub> is shown in Fig. 3a. The TEM image of Cu<sub>2</sub>O template (Fig. 3b) displays a polyhedron structure with a size of  $\sim$ 250 nm. As shown in Fig. 3c, the size of the internal voids of the as-prepared hollow cages is  $\sim$ 250 nm, which is inherited from the dimensions of the Cu<sub>2</sub>O templates. As evidenced in the TEM image (Fig. 3d), the morphology of the HFC-like nanostructure is excellently preserved after annealing at 250°C. The specific surface area of HFC-250 is approximately 245.5 m<sup>2</sup> g<sup>-1</sup>, which is substantially higher than those of HFC-300 (120 m<sup>2</sup> g<sup>-1</sup>) and HFC-400 (67.3 m<sup>2</sup> g<sup>-1</sup>). The nearly symmetric charge-discharge curves imply that the HFC-250 delivers high coulombic efficiency and low polarization (Fig. 3e). At 1 A g<sup>-1</sup> (shown in Fig. 3f), the HFC-250 electrode possesses the largest specific capacitance (948.9 F g<sup>-1</sup>), which is markedly larger than those of HFC Co(OH)<sub>2</sub> (400.7 F g<sup>-1</sup>), HFC-300 (489.9 F g<sup>-1</sup>), HFC-400 (297 F g<sup>-1</sup>), and Co<sub>3</sub>O<sub>4</sub>-common (151.3 F g<sup>-1</sup>) electrodes (2 mol L<sup>-1</sup> KOH). Furthermore, the HFC-250 exhibits superior rate performance (Fig. 3g) and good cycle stability.

### Nickel oxides

Nickel oxides have been widely studied in SCs field because of their high theoretical capacity (2573 F g<sup>-1</sup>), cost effectiveness, and environmental friendliness [94–99]. By an easy hydrothermal method, Hu *et al.* [100] designed and synthesized hierarchical NiO nanosheets/nanowires with Ni foam substrate. The specific capacitances of the electrodes are 1493 and 867 F g<sup>-1</sup> at 3 and 50 A g<sup>-1</sup> (6 mol L<sup>-1</sup> KOH), respectively, which are superior to those of the mesoporous NiO nanosheets (1250 and 633 F g<sup>-1</sup> at 3 and 50 A g<sup>-1</sup>, respectively). Furthermore, the unique hierarchical NiO nanosheet/nanowire electrodes exhibit good rate performance and good cycling stability.

Using a successive electrode-position method with ZnO nanorods as template on Ni foam, Cao *et al.* [101] synthesized 3D hierarchical NiO nanotube arrays. Fig. 4a shows the schematic for synthesizing this material. As seen in the SEM and TEM (Fig. 4b, c) images, the sample is consisted of interconnected branch nanoflakes ( $\sim$ 10 nm), and the diameter of nanotube is  $\sim$ 170 nm. Owing to the special hierarchical porous structure, the NiO nanotube arrays show high specific capacitances of 675 and 569 F g<sup>-1</sup> at 2 and 40 A g<sup>-1</sup> (1 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub>) (Fig. 4g), respectively. The pseudocapacitive performance of NiO nanotube arrays on Ni foil and Ni foam were also



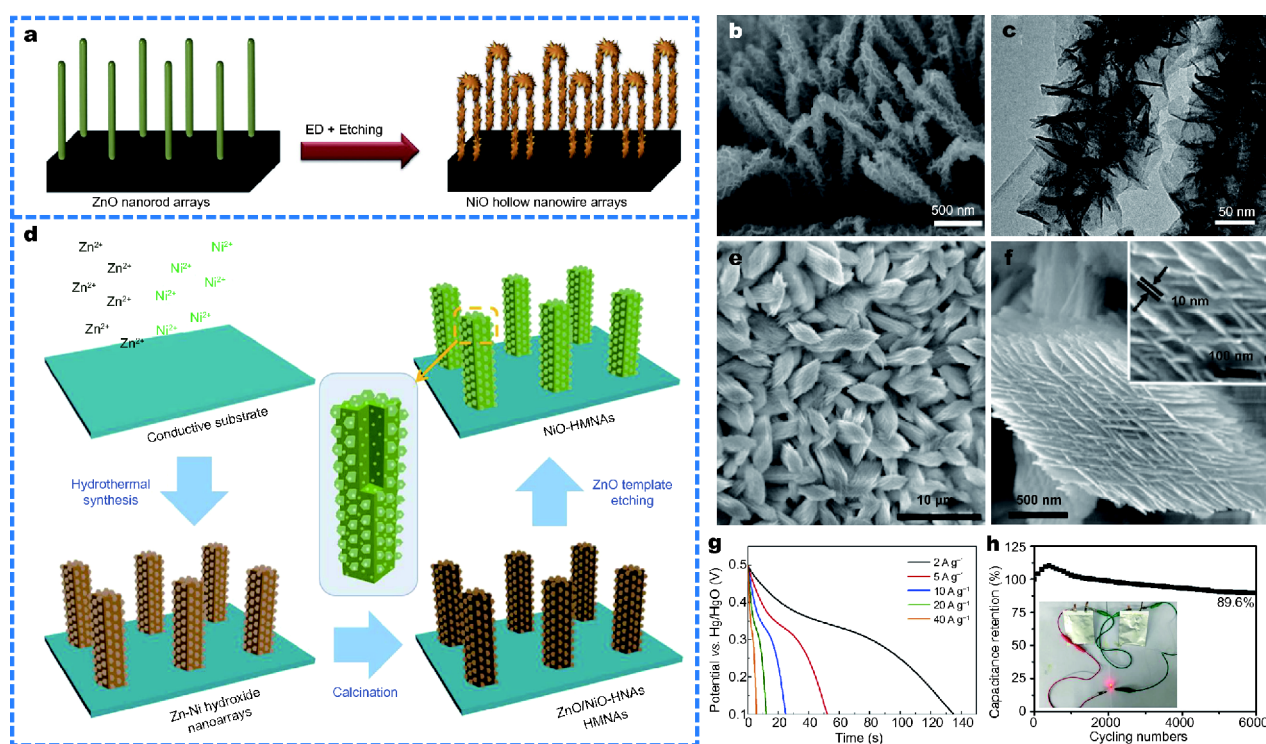
**Figure 3** (a) Schematic of the preparation of Co(OH)<sub>2</sub> and Co<sub>3</sub>O<sub>4</sub>. TEM images for (b) Cu<sub>2</sub>O template, (c) Co(OH)<sub>2</sub>, and (d) Co<sub>3</sub>O<sub>4</sub>. (e) Charge-discharge curves of the HFC-250 electrode. (f) Plots of the specific capacitance of Co(OH)<sub>2</sub>, HFC-250, HFC-300, HFC-400, and Co<sub>3</sub>O<sub>4</sub>-com. (g) Rate capability of the HFC-250 electrode when the current density was progressively varied. Reproduced with permission from Ref. [93]. Copyright 2015, the American Chemical Society.

compared. The specific capacitance of the NiO on the Ni foil is 495 F g<sup>-1</sup> at 2 A g<sup>-1</sup>, which is lower than that of the NiO on Ni foam (675 F g<sup>-1</sup> at 2 A g<sup>-1</sup>). The porous NiO arrays on Ni foam electrode demonstrate a low loss of 6.8% after 10,000 cycles at 2 A g<sup>-1</sup>. This excellent electrochemical performance can be ascribed to the hierarchical porous architecture with large reaction surface area and fast ion transfer. This synthesis method can potentially be applied to the fabrication of other TMO nanotube arrays.

Multi-shell self-assembled hollow structure materials are also investigated in SCs. Zhu *et al.* [102] designed and prepared single-, double-, and triple-shelled NiO (S-NiO, D-NiO, and T-NiO, respectively) hollow nanospheres by a controllable layer-by-layer self-assembly method with the calcination of Ni(OH)<sub>2</sub>/C precursors. The BET specific surface area of the D-NiO is approximately 92.99 m<sup>2</sup> g<sup>-1</sup>, which is higher than those of T-NiO (23.45 m<sup>2</sup> g<sup>-1</sup>) and S-NiO (61.63 m<sup>2</sup> g<sup>-1</sup>). The average

pore sizes for S-NiO, D-NiO, and T-NiO are 18.24, 7.04, and 12.30 nm, respectively. The electrochemical measurements indicate that the D-NiO possesses the highest specific capacitance of 612.5 F g<sup>-1</sup> compared with S-NiO (432.2 F g<sup>-1</sup>) and T-NiO (292.4 F g<sup>-1</sup>) at 0.5 A g<sup>-1</sup> (2 mol L<sup>-1</sup> KOH). The D-NiO also exhibits good cyclic performance, with capacitance retention exceeding 90% after 1,000 cycles.

Using a facile, low-cost, and environment-friendly template method, Liu *et al.* [103] successfully prepared hierarchical mesoporous NiO nanoarrays (NiO-HMNAs). The synthesis process of NiO-HMNAs is shown in Fig. 4d. The edge length of NiO-HMNAs is 1.6 μm (shown in Fig. 4e, f). The average thickness of NiO-HMNAs is ~10 nm (Fig. 4f, inset). As a battery-type electrode for hybrid SCs, the specific capacitance of NiO-HMNAs is 3114 F g<sup>-1</sup> at 5 mA cm<sup>-2</sup> (2 mol L<sup>-1</sup> KOH). Furthermore, the optimized hybrid SC device demonstrates a high energy density of 67.0 Wh kg<sup>-1</sup> at a power



**Figure 4** (a) Schematic of the preparation of hierarchical NiO nanotube arrays on Ni foam. (b) SEM image of NiO nanotube arrays on Ni foam. (c) TEM image of NiO nanotube. (d) Schematic of the preparation of NiO–HMNAs on Cu foam. (e) and (f) SEM images of NiO–HMNAs. (g) Discharge curves of NiO nanotube arrays on Ni foam. (h) Cycling performance of the hybrid SC device based on NiO–HMNAs. Reproduced with permission from Ref. [101]. Copyright 2014, Elsevier. (d–f, h) Reproduced with permission from Ref. [103]. Copyright 2016, Elsevier.

density of  $320 \text{ W kg}^{-1}$  and a good capacitance retention of 89.6% after 6,000 cycles (Fig. 4h). The ultrahigh specific capacitance of NiO–HMNAs is ascribed to the unique hierarchical mesoporous architecture.

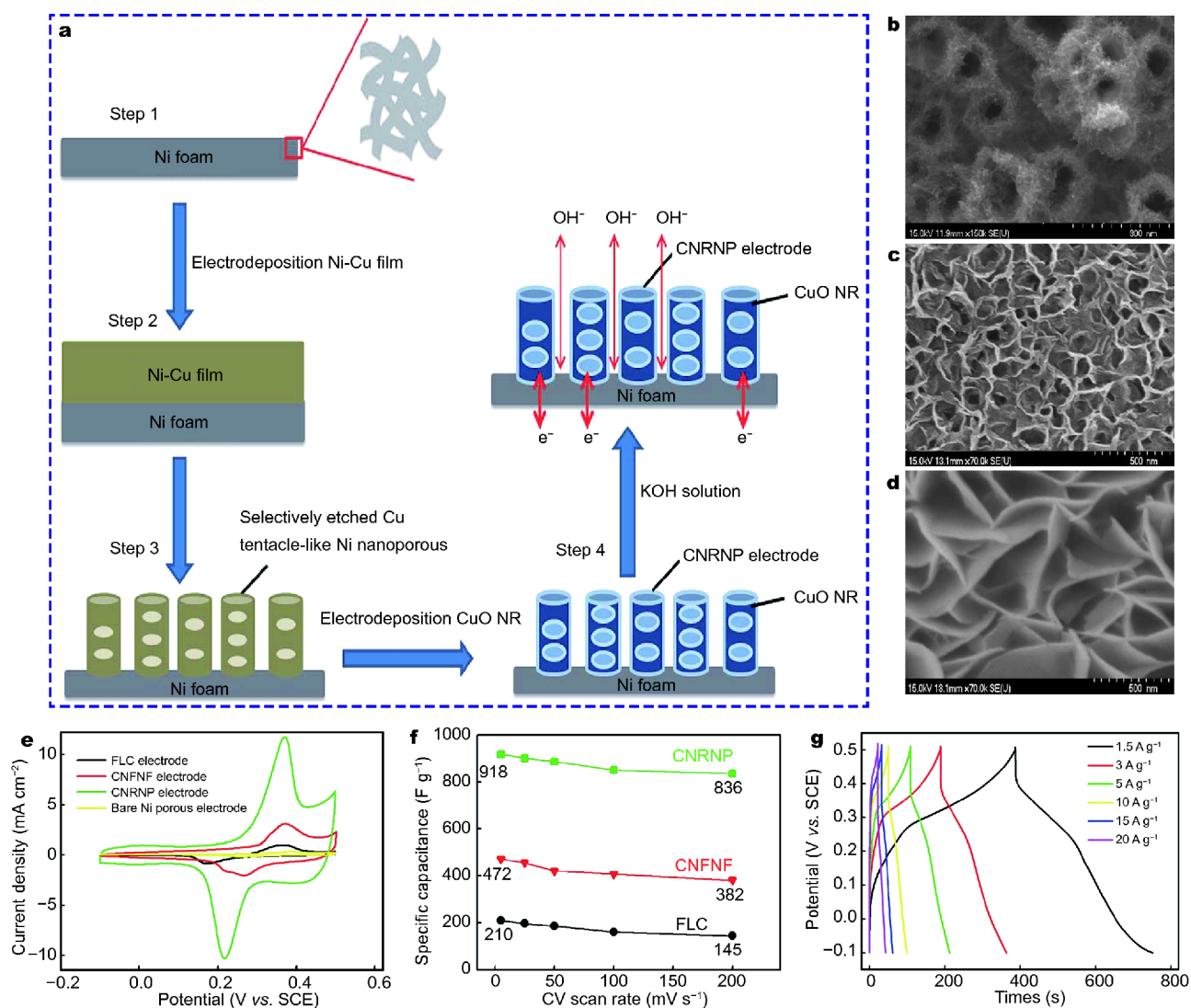
### Copper oxides

Copper oxide can be considered as another promising candidate for SCs because of its non-toxicity, abundance, and facile preparation [104,105]. Through a facile electrochemical process, 3D nanostructured CuO electrodes were prepared for SCs by Chen *et al.* (Fig. 5a, b) [106]. Due to its unique nanostructure, the as-prepared CuO nanoribbon-on-Ni-nanoporous/Ni foam (CNRNP) electrodes show excellent energy storage performance relative to a traditional electrode. Ni foam and flat Ni are also respectively used as substrate to fabricate general copper oxide samples. On the Ni foam, CuO nanoflakes (CNFNF) form a thick and uniform film, completely covering the Ni foam framework (Fig. 5c). On the flat Ni plate, the flake-like CuO (FLC) is formed (Fig. 5d). The specific capacitance of the CNRNP electrode is  $800 \text{ F g}^{-1}$  at  $200 \text{ mV s}^{-1}$  ( $3 \text{ mol L}^{-1}$  KOH), which retains 91%

compared with that at  $10 \text{ mV s}^{-1}$  (Fig. 5e, f). By contrast, the CNFNF and FLC electrodes deliver 81% and 69% of that at  $10 \text{ mV s}^{-1}$ , respectively. The symmetric triangular shape of charge–discharge curves indicates that the CNRNP possesses satisfactory pseudocapacitive behavior (Fig. 5g).

An easy and low-cost one-step surface oxidation process was applied by Zhao *et al.* [107] for the preparation of 3D flower-like CuO hierarchical structures grown on Cu foam. Given the innovative synthesis method and 3D connect/quasi-connect structures, this sample gains considerable attention as binder-free electrode material for SCs. The 3D flower-like CuO/Cu foam electrode could offer abundant active sites for redox reactions, effectively promote electrolyte penetration, enhance electronic conductivity, and shorten ion diffusion pathway. The specific capacitances of CuO are calculated to be  $1641.4$  and  $1266.7 \text{ mF cm}^{-2}$  at  $2$  and  $20 \text{ mA cm}^{-2}$  ( $5 \text{ mol L}^{-1}$  NaOH), respectively.

By an alkaline solution oxidation, Luo *et al.* [108] successfully synthesized CuO nanostructures with different surfactants (sodium dodecyl sulfate (SDS) and poly-



**Figure 5** (a) Schematic of the preparation of CNRNP electrode; SEM images of (b) CNRNP, (c) CNFNF, and (d) FLC; (e) CV curves of all samples at  $10 \text{ mV s}^{-1}$ ; (f) specific capacitance of all samples at different scan rates; (g) charge-discharge curves of CNRNP. Reproduced with permission from Ref. [106]. Copyright 2014, the Royal Society of Chemistry.

vinyl alcohol (PVA)). The CuO electrode obtained with SDS shows superior electrochemical performance because of its ultrathin nanoleaves, which constitute a flower-shaped nanostructure, and possesses specific capacitances of  $520$  and  $405 \text{ F g}^{-1}$  at  $1$  and  $60 \text{ A g}^{-1}$  ( $1 \text{ mol L}^{-1} \text{ KOH}$ ), respectively, and a capacitance retention of  $95.2\%$  after  $5,000$  cycles at  $1 \text{ A g}^{-1}$ .

### Bismuth oxides

Owing to abundant crystal morphologies and unique physical properties,  $\text{Bi}_2\text{O}_3$  has attracted extensive attention in SC field [109].  $\text{Bi}_2\text{O}_3$  presents five main polymorphic forms ( $\alpha$ -,  $\beta$ -,  $\gamma$ -,  $\delta$ -, and  $\omega$ - $\text{Bi}_2\text{O}_3$ ). Among these

forms, the high-temperature  $\delta$  and low-temperature  $\alpha$  phases are stable [110–112]. Gujar *et al.* first reported that  $\text{Bi}_2\text{O}_3$  thin film, as positive electrode material for SCs, possessed a low specific capacitance of only  $98 \text{ F g}^{-1}$  but exhibited high electrochemical reversibility [112].

Tong *et al.* [113] reported that hierarchical rippled  $\text{Bi}_2\text{O}_3$  nanobelts were synthesized *via* an electrode-position method. The  $\text{Bi}_2\text{O}_3$  nanobelts possess a width of  $250$ – $300 \text{ nm}$ , a length of  $1$ – $5 \mu\text{m}$ , and a thickness of  $10$ – $30 \text{ nm}$ . The intervals between the ripples are approximately  $15$ – $30 \text{ nm}$ . The BET specific surface area of hierarchical  $\text{Bi}_2\text{O}_3$  nanobelts sample ( $196 \text{ m}^2 \text{ g}^{-1}$ ) is 8 times of that of  $\text{Bi}_2\text{O}_3$  nanobelts sample with smooth surfaces ( $24 \text{ m}^2 \text{ g}^{-1}$ ).

The specific capacitance of the hierarchical rippled  $\text{Bi}_2\text{O}_3$  nanobelts is  $250 \text{ F g}^{-1}$  at  $100 \text{ mV s}^{-1}$  ( $1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ ), which is remarkably larger than the  $\text{Bi}_2\text{O}_3$  nanobelts with smooth surfaces ( $61 \text{ F g}^{-1}$ ).

An easy one-step precipitation approach with the addition of diverse surfactants was used by Yuan's group for the synthesis of rod-like  $\text{Bi}_2\text{O}_3$  [114]. The surfactants with various chain structures can effectively regulate and control the morphologies of  $\text{Bi}_2\text{O}_3$  products. The  $\text{Bi}_2\text{O}_3$  sample synthesized using P123 surfactant as electrode material was investigated. The sample exhibits a large specific capacitance of  $1350 \text{ F g}^{-1}$  at  $0.1 \text{ A g}^{-1}$  ( $6 \text{ mol L}^{-1} \text{ KOH}$ ), excellent rate performance (71.4% retention from 0.1 to  $2 \text{ A g}^{-1}$ ), and an outstanding cycle performance (only 2.4% capacitance fade after 1,000 cycles).

### Nickel cobalt oxides

Bimetallic oxides usually offer higher electrochemical activity than single metal oxides [115–117]. Nickel cobaltite exhibits excellent electrochemical performance because of richer redox reaction between nickel and cobalt ions [118]. A variety of nickel cobaltite materials with different morphologies, such as NPs [119], nanowires [120,121], urchin-like shape [122], and hollow spheres [123], have been studied as electrode materials for SCs.

To shorten the synthesis time, Xiao *et al.* [124] reported a template-free microwave-assisted heating reflux method to prepare 3D hierarchical flower-shaped  $\text{NiCo}_2\text{O}_4$  microspheres. The  $\text{NiCo}_2\text{O}_4$  microspheres are constituted of numerous flower-shaped nanostructures. The flower-shaped  $\text{NiCo}_2\text{O}_4$  microspheres demonstrate a high specific capacitance of  $1006 \text{ F g}^{-1}$  at  $1 \text{ A g}^{-1}$  ( $6 \text{ mol L}^{-1} \text{ KOH}$ ) and good cycle performance (retention of 93.2% after 1,000 cycles at  $8 \text{ A g}^{-1}$ ).

The design and preparation of novel nanomaterials have gradually become the core research in optimizing pseudocapacitive performance. Li *et al.* [125] reported that the  $\text{NiCo}_2\text{O}_4$  multiple hierarchical structures (MHSs) composed of two-dimensional (2D) nanosheets and one-dimensional (1D) nanowires were directly anchored on Ni foam (Fig. 6a). First, the  $\text{NiCo}_2\text{O}_4$  nanowires (NCO1) that uniformly covered the substrate were formed by a hydrothermal process followed by annealing treatment. After that, by a second hydrothermal process, the NCO1 was transformed into  $\text{NiCo}_2\text{O}_4$  MHSs, which was named as NCO2. The nanowire was found to be superior over the high-dimensional nanosheet in the growth order; thereby effectively promoting the integration of these different nanostructures into the  $\text{NiCo}_2\text{O}_4$  MHSs. As shown in Fig. 6b, c, the  $\text{NiCo}_2\text{O}_4$  MHSs with diameters of

about 4–6  $\mu\text{m}$  were obtained. All microspheres possess a 3D structure, in which the 2D nanosheets form the skeleton of microspheres, while the 1D nanowires surround the nanosheet. Given the favorable mesoporous architecture and large specific surface area, the sample NCO2 ( $\text{NiCo}_2\text{O}_4$  MHSs) shows the highest specific capacitance of  $2623.3 \text{ F g}^{-1}$  at  $1 \text{ A g}^{-1}$  ( $3 \text{ mol L}^{-1} \text{ KOH}$ ) (Fig. 6d). A capacity retention of 68% can be achieved from  $1 \text{ A g}^{-1}$  to  $40 \text{ A g}^{-1}$ . The sample also displays good stability with 94% retention after 3,000 cycles at  $10 \text{ A g}^{-1}$ .

By a mild solution approach with polymeric nanotubes (PNT) as the template, Yu *et al.* [126] successfully fabricated hierarchical  $\text{NiCo}_2\text{O}_4$  nanotubes composed of nanosheets. Fig. 6e displays the SEM image of  $\text{NiCo}_2\text{O}_4$  nanotubes obtained after calcination of the Ni-precursor@PNT composite at  $400^\circ\text{C}$ . As shown in Fig. 6f, the mesoporous  $\text{NiCo}_2\text{O}_4$  nanosheet–nanotube structures possess hierarchical external construction and hollow internal structure with a diameter of approximately 100 nm. When tested at 2, 4, 8, 10, 20, and  $40 \text{ A g}^{-1}$  ( $2 \text{ mol L}^{-1} \text{ KOH}$ ), the  $\text{NiCo}_2\text{O}_4$  nanotube electrodes show high specific capacitances of 1468, 1352, 1233, 1178, 1020, and  $672 \text{ F g}^{-1}$ , respectively. At  $10 \text{ A g}^{-1}$ , the specific capacitance is  $1178 \text{ F g}^{-1}$  in the first cycle. The specific capacitance gradually decreases to  $1168 \text{ F g}^{-1}$  after 3,000 cycles, resulting in only 0.8% loss of overall capacitance. Furthermore, the  $\text{NiCo}_2\text{O}_4$  nanotubes show virtually 100% of the coulombic efficiency during the whole cycle (Fig. 6g). This excellent performance of the  $\text{NiCo}_2\text{O}_4$  nanotubes is ascribed to the porous and hierarchical structures, which provide more effective contact areas between the active materials and electrolyte ions. Moreover, the wide-open ends of the  $\text{NiCo}_2\text{O}_4$  nanotubes provide extra paths for the electrolyte.

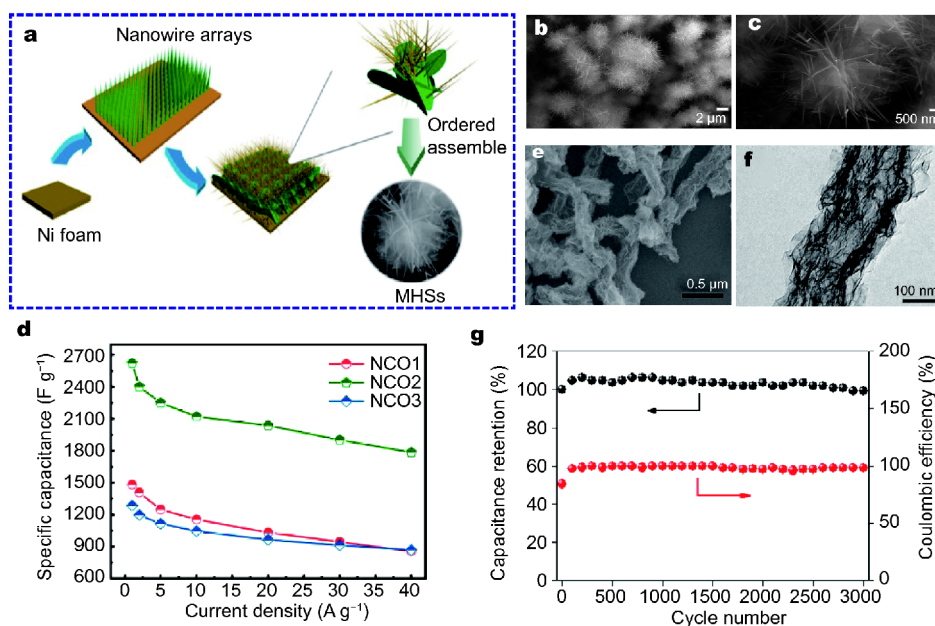
### Zinc vanadium oxides

Cao *et al.* [127] designed a simple and template-free approach to fabricate hierarchical nanospheres (NHNs) of  $\text{ZnV}_2\text{O}_4$ . As shown in Fig. 7a, b, these nanospheres are composed of extremely thin nanosheets. Fig. 7c demonstrates the crystal geometry of spinel oxide  $\text{ZnV}_2\text{O}_4$ . Fig. 7d shows that the specific capacitances of  $\text{ZnV}_2\text{O}_4$  NHNs are 385, 360, 324, and  $272 \text{ F g}^{-1}$  at current densities of 0.5, 1, 2, and  $4 \text{ A g}^{-1}$ , respectively. Furthermore, the  $\text{ZnV}_2\text{O}_4$  NHNs electrode exhibits good cycle stability with 89% of capacity retention after 1,000 cycles at  $1 \text{ A g}^{-1}$ .

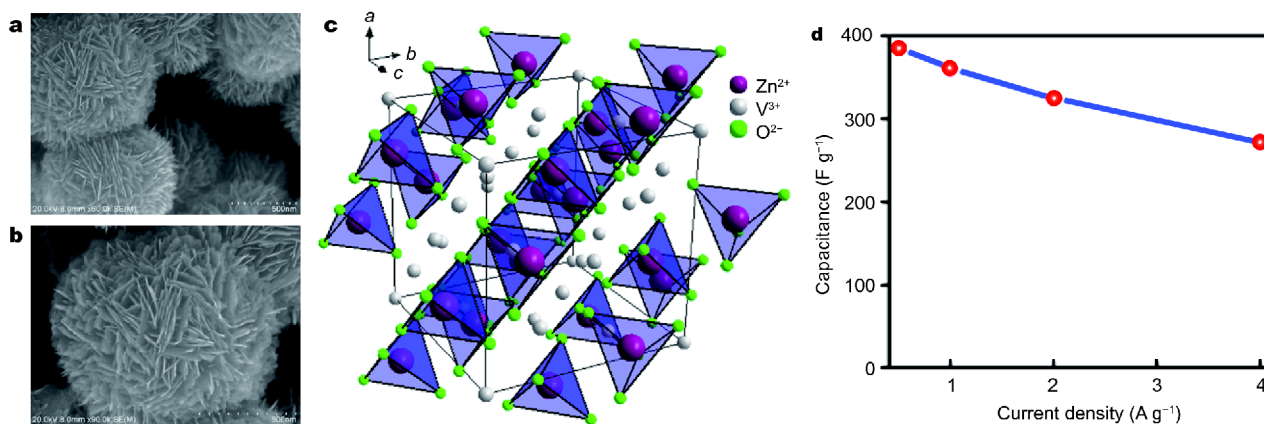
## HIERARCHICALLY NANOSTRUCTURED COMPOSITES BASED ON TMOs FOR SCs

Multiphase composites based on TMOs could effectively





**Figure 6** (a) Schematic of the preparation of NiCo<sub>2</sub>O<sub>4</sub> MHSs; (b and c) FESEM images of the NiCo<sub>2</sub>O<sub>4</sub> MHSs (NCO2) on Ni foam; (d) specific capacitance obtained from the discharge curves; (e) SEM image and (f) TEM image of the hierarchical NiCoO<sub>2</sub> nanosheets; (g) cycling performance of NiCoO<sub>2</sub> at 10 A g<sup>-1</sup>. (a, d) Reproduced with permission from Ref. [125]. Copyright 2014, the American chemical Society. (e–g) Reproduced with permission from Ref. [126]. Copyright 2014, Elsevier.



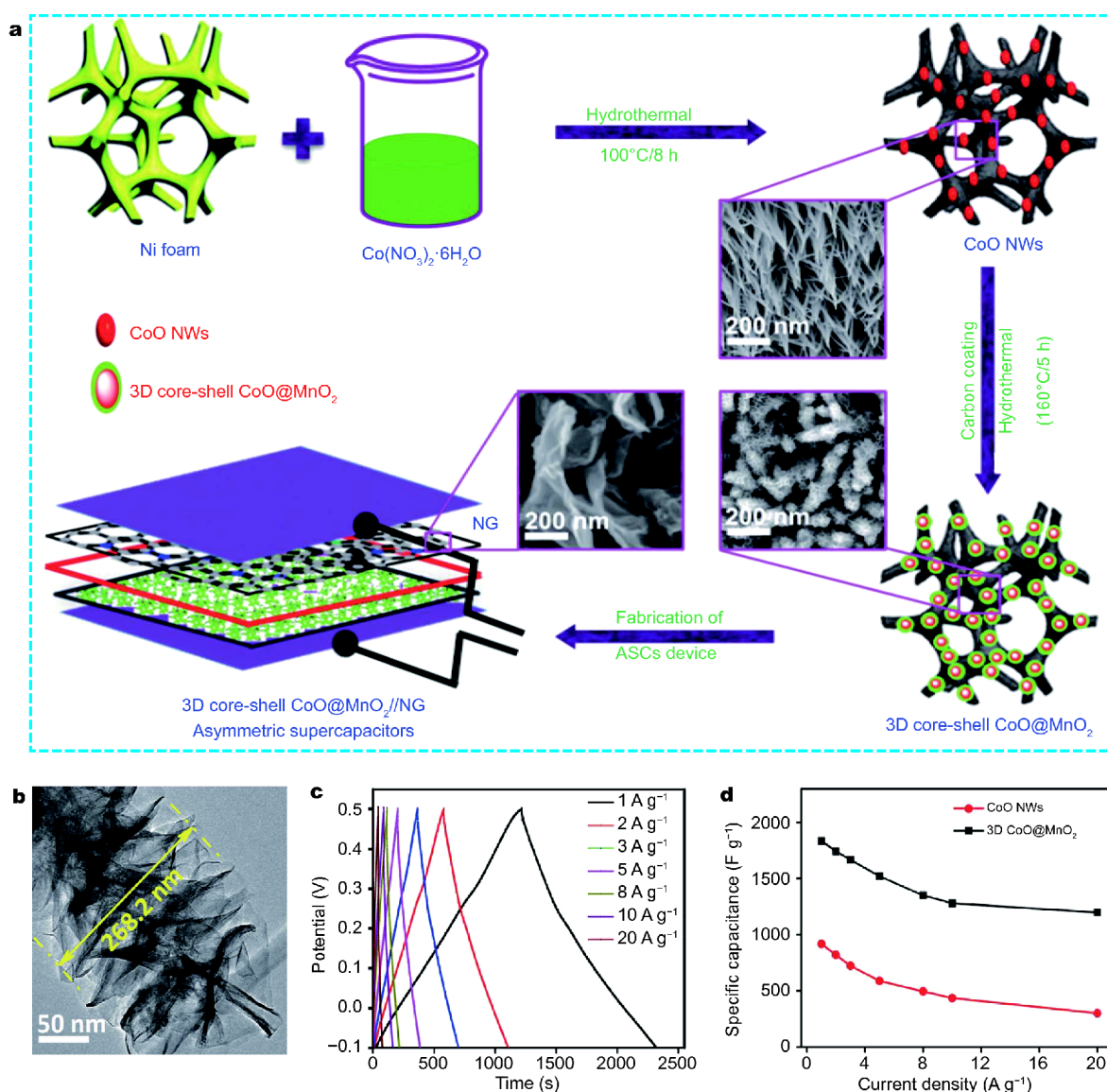
**Figure 7** (a and b) SEM images of ZnV<sub>2</sub>O<sub>4</sub> NHNs; (c) crystal structure of spinel ZnV<sub>2</sub>O<sub>4</sub> with corresponding atoms; (d) capacitance as a function of current density. Reproduced with permission from Ref. [127]. Copyright 2014, the American Chemical Society.

improve the specific capacitance and cycling performance of the devices compared with single-phase TMOs because of the complex chemical compositions and the synergetic effect of both individual components [128–135]. In the following section, four types of composites were introduced, namely: 1) composites of manganese oxides and other TMOs; 2) composites of gold NP-doped TMOs; 3) composites of carbon materials and TMOs; and 4)

other forms of TMOs composites.

#### Composites of manganese oxides and other TMOs

Lee *et al.* [136] designed and synthesized binder-free 3D CoO@MnO<sub>2</sub> core-shell nanohybrids by using a facile method (shown in Fig. 8a). The 3D CoO@MnO<sub>2</sub> core-shell structure has a diameter of 268 nm (Fig. 8b). The 3D CoO@MnO<sub>2</sub> core-shell nanohybrid electrode delivers

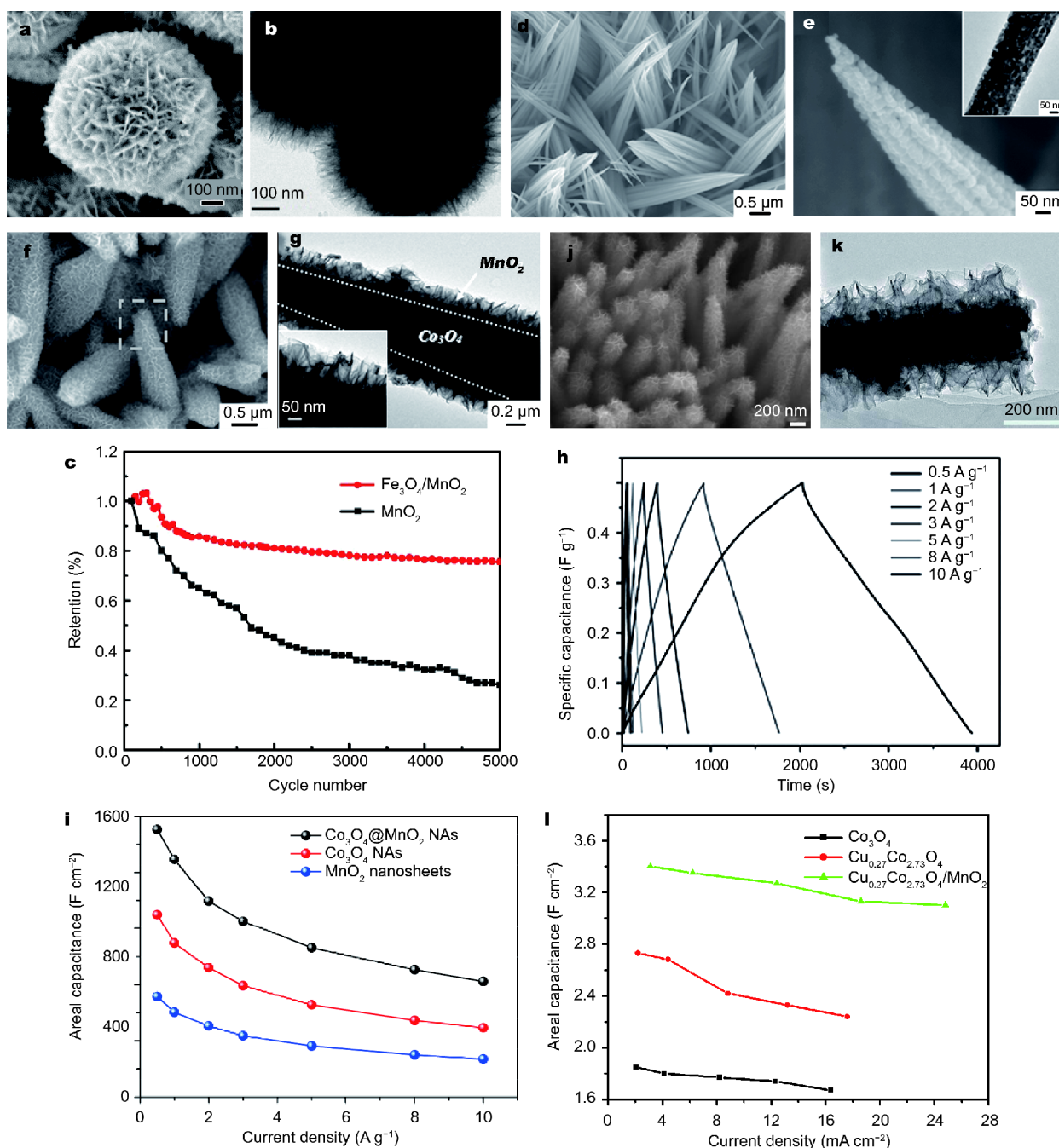


**Figure 8** (a) Schematic of the preparation of 3D CoO@MnO<sub>2</sub> nano hybrid; (b) TEM image of the 3D CoO@MnO<sub>2</sub>; (c) charge–discharge curves of the CoO@MnO<sub>2</sub>; (d) cycle stabilities of the 3D CoO@MnO<sub>2</sub> core–shell nano hybrid and CoO NWs at 5 A g<sup>-1</sup>. Reproduced with permission from Ref. [136]. Copyright 2017, the Royal Society of Chemistry.

good electrochemical performance with high specific capacitances (1835 and 1198 F g<sup>-1</sup> at 1 and 20 A g<sup>-1</sup>) (6 mol L<sup>-1</sup> KOH) (Fig. 8c, d), and outstanding cycle performance (97.7% capacitance retention after 10,000 cycles at 1 A g<sup>-1</sup>). When this 3D CoO@MnO<sub>2</sub> core–shell nano hybrid was used as cathode and assembled into an asymmetric SCs combined with a N-doped graphene anode, the formed asymmetric SCs device shows a high specific capacitance of 191 F g<sup>-1</sup> at 1 A g<sup>-1</sup> and good cycle performance with 86.8% retention after 10,000 cycles. The

device presents an energy density of about 85.9 W h kg<sup>-1</sup> at a power density of 852.4 W kg<sup>-1</sup>.

Meng *et al.* [137] fabricated hierarchically densely packed porous MnO<sub>2</sub> microspheres doped with Fe<sub>3</sub>O<sub>4</sub> NPs through a one-step low-cost ultrasound-assisted method. The SEM and TEM images (Fig. 9a, b) show that the sample owns a unique hierarchical nanostructure. The microsphere is composed of numerous randomly interconnected nanoflakes. The Fe<sub>3</sub>O<sub>4</sub>–MnO<sub>2</sub> electrode shows a capacitance of 367.4 F g<sup>-1</sup> at 100 mV s<sup>-1</sup> (1 mol L<sup>-1</sup>



**Figure 9** (a) SEM and (b) TEM images of the  $\text{Fe}_3\text{O}_4\text{-MnO}_2$  sample; (c) capacitance retention at  $5 \text{ A g}^{-1}$  over 5,000 cycles; (d, e) SEM images of the  $\text{Co}_3\text{O}_4$  NAs (the inset shows TEM image of the  $\text{Co}_3\text{O}_4$  NAs); (f, g) SEM and TEM images of  $\text{Co}_3\text{O}_4@/\text{MnO}_2$  NAs. (h) Charge-discharge curves of the  $\text{Co}_3\text{O}_4@/\text{MnO}_2$  composite. (i) Current density dependence of the specific capacitance of the  $\text{MnO}_2$  nanosheets,  $\text{Co}_3\text{O}_4$  NAs and  $\text{Co}_3\text{O}_4@/\text{MnO}_2$  NAs. (j, k) SEM and TEM images of  $\text{Cu}_{0.27}\text{Co}_{2.73}\text{O}_4/\text{MnO}_2$ ; (l) the specific capacitances of the three electrodes as a function of current density. (a–c) Reproduced with permission from Ref. [137]. Copyright 2014, the American Chemical Society. (d–i) Reproduced with permission from Ref. [138]. Copyright 2014, Wiley-VCH. (j–l) Reproduced with permission from Ref. [139]. Copyright 2015, the Royal Society of Chemistry.

$\text{Na}_2\text{SO}_4$ ). The capacitance retention of the  $\text{Fe}_3\text{O}_4\text{-MnO}_2$  composite is markedly superior to that of single  $\text{MnO}_2$  (Fig. 9c). The good electrochemical performance of the

$\text{Fe}_3\text{O}_4\text{-MnO}_2$  sample is attributed to its unique hierarchical nanostructure, in which high-number-density and isolated  $\text{Fe}_3\text{O}_4$  NPs are distributed in the interior of

MnO<sub>2</sub>.

Cheng *et al.* [138] fabricated a hierarchical porous Co<sub>3</sub>O<sub>4</sub>@MnO<sub>2</sub> nanoneedle arrays (Co<sub>3</sub>O<sub>4</sub>@MnO<sub>2</sub> NAs) on Ni foam *via* a hydrothermal method. The synthesis of Co<sub>3</sub>O<sub>4</sub>@MnO<sub>2</sub> NAs can be divided into four steps. First, through a modified hydrothermal process, Co(OH)<sub>2</sub>CO<sub>3</sub> is directly grown on Ni foam substrate. Further heat treatment enables the formation of porous Co<sub>3</sub>O<sub>4</sub> nanostructures. Afterward, the porous Co<sub>3</sub>O<sub>4</sub> nanoneedles are coated with a thin carbon nanolayer. Finally, the Co<sub>3</sub>O<sub>4</sub>@MnO<sub>2</sub> NAs are obtained *via* the formation of MnO<sub>2</sub> nanosheets through a reaction between KMnO<sub>4</sub> and carbon. As shown in Fig. 9d, the Co<sub>3</sub>O<sub>4</sub> nanoneedles stand on the Ni foam substrate. Each nanoneedle consists of numerous small NPs accumulating with each other, forming a nanoporous structure (shown in Fig. 9e). Fig. 9f, g show the SEM and TEM images of Co<sub>3</sub>O<sub>4</sub>@MnO<sub>2</sub> NAs. Thin MnO<sub>2</sub> nanosheets are covered on the surface of Co<sub>3</sub>O<sub>4</sub> nanoneedles, forming a core-shell hierarchical nanostructure. The galvanostatic charge-discharge curves of the Co<sub>3</sub>O<sub>4</sub>@MnO<sub>2</sub> NAs investigated at 0.5–10 A g<sup>-1</sup> (1 mol L<sup>-1</sup> LiOH) are shown in Fig. 9h. The sample displays relatively high specific capacitances of 1905.4, 1693.2, 1396, 1253.4, 1062, 905.6, and 823 F g<sup>-1</sup> at 0.5, 1, 2, 3, 5, 8, and 10 A g<sup>-1</sup>, respectively. Fig. 9i shows that the performance of the Co<sub>3</sub>O<sub>4</sub>@MnO<sub>2</sub> NAs is obviously better than those of the individual MnO<sub>2</sub> nanosheets and Co<sub>3</sub>O<sub>4</sub> nanoneedles. Furthermore, the Co<sub>3</sub>O<sub>4</sub>@MnO<sub>2</sub> composite materials possess a high energy density of 66.2 W h kg<sup>-1</sup> at a power density of 0.25 kW kg<sup>-1</sup>.

A hydrothermal and post-heat treatment method was employed by Yin *et al.* [139] for the preparation of hierarchical Cu<sub>0.27</sub>Co<sub>2.73</sub>O<sub>4</sub>/MnO<sub>2</sub> nanorod arrays. The MnO<sub>2</sub> nanoflakes homogeneously grow on Cu<sub>0.27</sub>Co<sub>2.73</sub>O<sub>4</sub> nanorods which are grown on Ni foam, and the average diameter of the composites is approximately 250–300 nm (shown in Fig. 9j, k). The specific capacitances of Cu<sub>0.27</sub>Co<sub>2.73</sub>O<sub>4</sub> and Cu<sub>0.27</sub>Co<sub>2.73</sub>O<sub>4</sub>/MnO<sub>2</sub> are 2.24 F cm<sup>-2</sup> at 17.6 mA cm<sup>-2</sup> and 3.1 F cm<sup>-2</sup> at 24.8 mA cm<sup>-2</sup>, respectively (Fig. 9l). The specific capacitance of Co<sub>3</sub>O<sub>4</sub> at 16.4 mA cm<sup>-2</sup> is 1.67 F cm<sup>-2</sup>, which is markedly lower than those of Cu<sub>0.27</sub>Co<sub>2.73</sub>O<sub>4</sub> and Cu<sub>0.27</sub>Co<sub>2.73</sub>O<sub>4</sub>/MnO<sub>2</sub> electrodes. As the current density increases from 2.2 to 17.6 mA cm<sup>-2</sup>, the capacity of Cu<sub>0.27</sub>Co<sub>2.73</sub>O<sub>4</sub> remains at ~82.1%. For Cu<sub>0.27</sub>Co<sub>2.73</sub>O<sub>4</sub>/MnO<sub>2</sub>, a better rate capability with approximately 91.2% capacitance retention can be observed as the current density increases from 3.1 to 24.8 mA cm<sup>-2</sup>. The homogeneously aligned structure of Cu<sub>0.27</sub>Co<sub>2.73</sub>O<sub>4</sub> nanorods with planar tips and a rough surface can effectively control the aggregation of active

materials and shorten the pathway for ion transportation, further resulting in large areal capacitance and superior rate capability. These results demonstrate the opportunity of the potential candidate as binder-free electrodes applied in SCs and show great potential in exploring higher areal capacitance for miniaturized devices.

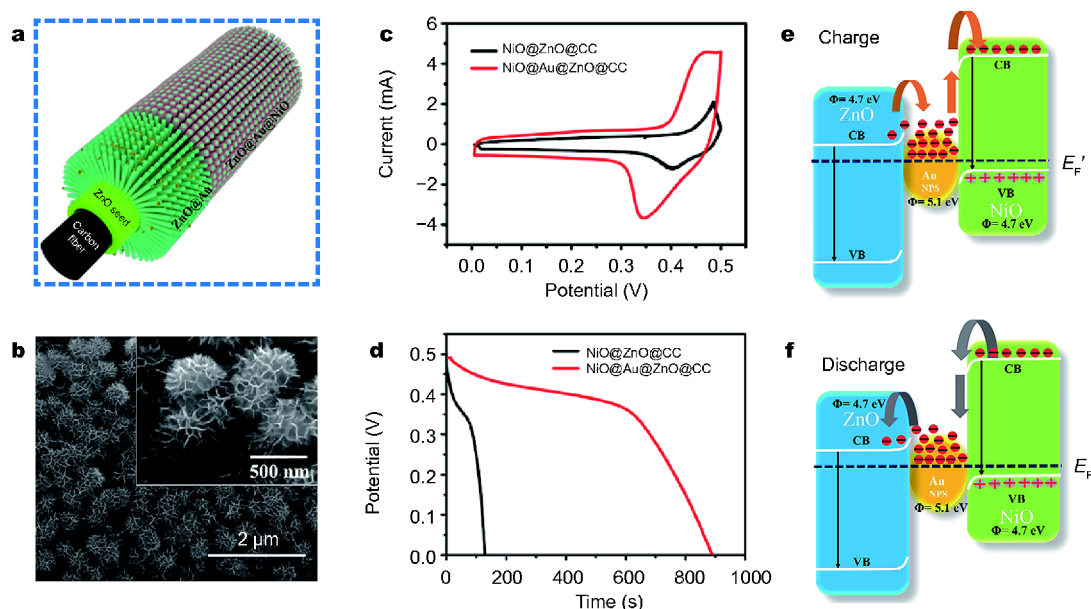
Liu *et al.* [140] prepared hierarchical NiCo<sub>2</sub>O<sub>4</sub>@MnO<sub>2</sub> core-shell nanosheet array composites on Ni foam by a two-step hydrothermal method. Owing to the unique nanoarchitecture, the NiCo<sub>2</sub>O<sub>4</sub>@MnO<sub>2</sub> core-shell nanosheet arrays display a high areal capacitance of 2.39 F cm<sup>-2</sup>, (1595.1 F g<sup>-1</sup>) at 3 mA cm<sup>-2</sup> (1 mol L<sup>-1</sup> NaOH). However, the areal capacitance of pure NiCo<sub>2</sub>O<sub>4</sub> nanosheet arrays was calculated to be only 1.50 F cm<sup>-2</sup> at 3 mA cm<sup>-2</sup>. The NiCo<sub>2</sub>O<sub>4</sub>@MnO<sub>2</sub> sample also exhibits good cycle performance (92.6% retention after 2000 cycles at 40 mA cm<sup>-2</sup>), which is superior to that of the pristine NiCo<sub>2</sub>O<sub>4</sub> nanosheet sample. The results show that the growth of MnO<sub>2</sub> nanosheets on NiCo<sub>2</sub>O<sub>4</sub> nanosheets is a viable approach to increase the capacitive properties of materials and simultaneously improve the cycling performance of SCs.

By a facile two-step electro-deposition process, Zhang *et al.* [141] successfully synthesized a 3D hierarchical NiCo<sub>2</sub>O<sub>4</sub>@MnO<sub>2</sub> hybrid nanomaterial grown on stainless steel mesh. The specific capacitance of NiCo<sub>2</sub>O<sub>4</sub>@MnO<sub>2</sub> at 2 A g<sup>-1</sup> is 688.4 F g<sup>-1</sup>, which is markedly higher than those of MnO<sub>2</sub> (336.6 F g<sup>-1</sup>) and NiCo<sub>2</sub>O<sub>4</sub> (241 F g<sup>-1</sup>). The NiCo<sub>2</sub>O<sub>4</sub>@MnO<sub>2</sub> shows a high specific capacitance of 913.6 F g<sup>-1</sup> at 0.5 A g<sup>-1</sup> and a capacitance retention of 87.1% after 3,000 cycles. Furthermore, the asymmetric SCs device with a large voltage window of 1.5 V is assembled by using NiCo<sub>2</sub>O<sub>4</sub>@MnO<sub>2</sub> sample as the cathode and activated carbon as the anode. The device achieves an energy density of 37.5 W h kg<sup>-2</sup> at a power density of 187.5 W kg<sup>-1</sup>.

### Composites of gold NP-doped TMOs

TMOs doped with Au NPs are highly active and function as selective catalysts for a variety of chemical reactions [142,143]. The design of the TMOs composites with Au nanoparticles is demonstrated to be another efficient approach to enhance the electrochemical performance of TMOs as SC electrodes [144]. Wang *et al.* [145] designed and synthesized an Au–NiO composite that exhibited a markedly improved rate performance on SCs. The specific capacitance of the Au–NiO electrode at 20 A g<sup>-1</sup> is 619 F g<sup>-1</sup>, which is markedly higher than that of pure NiO electrode (216 F g<sup>-1</sup>).

You *et al.* [146] successfully synthesized mono-



**Figure 10** (a) Schematic illustration for the fabrication of hierarchical ZnO@Au@NiO nanocomposite; (b) SEM images of ZnO@Au@NiO; (c) CV curves of two samples; (d) discharge curves of two samples; (e and f) energy level diagrams at the interface of ZnO–Au–NiO during charge–discharge process. Reproduced with permission from Ref. [151]. Copyright 2015, the American Chemical Society.

dispersed dumbbell-like Au–Fe<sub>3</sub>O<sub>4</sub> NPs with different sizes (5/14, 5/21, 7/14, and 7/21 nm Au–Fe<sub>3</sub>O<sub>4</sub> NPs). The specific capacitance of 7/14 nm Au–Fe<sub>3</sub>O<sub>4</sub> NPs at 1 A g<sup>-1</sup> is 464 F g<sup>-1</sup> (1 mol L<sup>-1</sup> KOH), which is markedly higher than that of pure Fe<sub>3</sub>O<sub>4</sub> NPs (160 F g<sup>-1</sup>). The 7/14 nm Au–Fe<sub>3</sub>O<sub>4</sub> composite exhibits a higher capacitance retention of 86.4% after 1,000 cycles at 10 A g<sup>-1</sup> than that of pure Fe<sub>3</sub>O<sub>4</sub> NP electrode (72.8% retention of initial capacitance). The above capacitive enhancement can be ascribed to the electron transfer increase induced by gold across the dumbbell-like NPs.

A simple and controllable electrochemical deposition process was employed by Hu's groups to synthesize the 3D hierarchical heterostructure of MnO<sub>2</sub> nanosheets and nanorods directly grown on porous Au-coated Co<sub>3</sub>O<sub>4</sub> nanowall array, and to assemble a sandwich construction of Co<sub>3</sub>O<sub>4</sub>@Au@MnO<sub>2</sub> [147]. Owing to the unique sandwich construction, each component is efficiently used for energy reaction. The specific capacitance of the Co<sub>3</sub>O<sub>4</sub>@Au@MnO<sub>2</sub> nanosheet hierarchical heterostructures (Co<sub>3</sub>O<sub>4</sub>@Au@MnO<sub>2</sub> (NSs) HHs) is 1532.4 F g<sup>-1</sup> at 1 A g<sup>-1</sup> (1 mol L<sup>-1</sup> LiOH), which is higher than those of the Au-coated Co<sub>3</sub>O<sub>4</sub> nanowall arrays (1046.6 F g<sup>-1</sup>) and Co<sub>3</sub>O<sub>4</sub>@Au@MnO<sub>2</sub> nanorod hierarchical heterostructures (Co<sub>3</sub>O<sub>4</sub>@Au@MnO<sub>2</sub> (NRs) HHs) (1292.9 F g<sup>-1</sup>). The Co<sub>3</sub>O<sub>4</sub>@Au@MnO<sub>2</sub> (NSs) HHs also exhibit superior cycling performance (with virtually no degradation after 5,000

cycles). Furthermore, the presented results of the Co<sub>3</sub>O<sub>4</sub>@Au@MnO<sub>2</sub> (NSs) HHs are larger than those of the reported Co<sub>3</sub>O<sub>4</sub> or MnO<sub>2</sub>-based heterostructures, such as MnO<sub>2</sub>/Mn/MnO<sub>2</sub> nanotube arrays (937 F g<sup>-1</sup> at 1.5 A g<sup>-1</sup>) [148], Zn<sub>2</sub>SO<sub>4</sub>@MnO<sub>2</sub> nanorods (642.3 F g<sup>-1</sup> at 1 A g<sup>-1</sup>) [149], and Co<sub>3</sub>O<sub>4</sub>/NiO nanowire arrays (853 F g<sup>-1</sup> at 2 A g<sup>-1</sup>) [150]. Thus, the Co<sub>3</sub>O<sub>4</sub>@Au@MnO<sub>2</sub> (NSs) HHs could be recognized as promising materials for SCs.

Yan *et al.* [151] designed and synthesized a hierarchical ZnO@Au@NiO nanocomposite as the electrode of SCs (Fig. 10a,b). First, ZnO nanowires arrays were grown on carbon nanofibers of carbon cloth. Then, a small quantity of Au nanoparticles was covered on ZnO nanowires. Subsequently, NiO nanosheets were uniformly grown on the surface of the Au-modified ZnO nanowires to obtain the ZnO@Au@NiO composites. The ZnO/Au/NiO electrode possesses a larger area in the CV curve, suggesting superior electrochemical performance to that of ZnO/NiO nanorods (shown in Fig. 10c). The areal capacitance of the ZnO@Au@NiO nanocomposite is calculated to be 3.50 F cm<sup>-2</sup> at 2 mA cm<sup>-2</sup> (1 mol L<sup>-1</sup> KOH), whereas the ZnO@NiO electrode only shows an areal capacitance of 0.42 F cm<sup>-2</sup> under the same condition (Fig. 10d). The ZnO@Au@NiO nanocomposite electrode demonstrates good cyclic stability with approximately 80.3% capacitance retention after 4,000 continuous cycles at 30 mA cm<sup>-2</sup>. The enhanced electrochemical property is

mainly ascribed to the decoration of Au nanoparticles. On one hand, Au nanoparticles can accelerate electron conduction. On the other hand, electrons can be temporarily trapped and accumulated at the Fermi level ( $E_F$ ) due to the localized Schottky barrier at Au/NiO interface during charge process until filling the gap between ZnO and NiO (Fig. 10e) [151]. Thus, more electrons can be released during discharge process (Fig. 10f).

### Composites of carbon materials and TMOs

For pseudocapacitors, surface oxidation–reduction reaction of metal oxides can result in higher specific capacitances [152]. Nanostructured carbon materials are generally utilized as EDLC electrodes, demonstrating their superior long-term electrochemical stability [153]. Thus, considerable efforts have been made to enhance the SC performance by creating composites of TMOs and carbon materials, such as TMOs/graphene and TMOs/carbon nanofibers (CFs) [154–167]. The synthesized multi-component composites can maximize the benefits from all components [154–169].

Wang *et al.* [170] designed and fabricated two types of hierarchical core–shell fiber-based electrodes, including MnO<sub>2</sub>/reduced graphene oxide (RGO)/CF and 3D porous graphene hydrogel-wrapped Cu wire (GH/CW). The specific areal capacitance and volumetric capacitance of the MnO<sub>2</sub>/RGO/CF electrode are 205.7 mF cm<sup>-2</sup> and 13.7 F cm<sup>-3</sup> at 0.5 mA cm<sup>-2</sup> (1 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub>), respectively, and both values are considerably larger than those of MnO<sub>2</sub>/CF (178.3 mF cm<sup>-2</sup> and 11.8 F cm<sup>-3</sup>) and RGO/CF (1.6 mF cm<sup>-3</sup> and 0.1 F cm<sup>-3</sup>). The results indicate that the synergistic effect and the interactions between the RGO nanosheets and MnO<sub>2</sub> nanoflakes in the MnO<sub>2</sub>/RGO/CF electrode markedly increase the total capacitive performance. The specific capacitance of the MnO<sub>2</sub>/RGO/CF electrode remains at 73% from 13.7 to 10 F cm<sup>-3</sup>. Owing to the synergistic effects of different components in nanohybrid fiber electrodes, the asymmetric SC device with MnO<sub>2</sub>/graphene/CF as the cathode and GH/CW as the anode shows a high areal energy density of 18.1 μW h cm<sup>-2</sup> and a volumetric energy density of 0.9 mW h cm<sup>-3</sup> in a voltage range of 0–1.6 V. Moreover, the asymmetric SC also shows an energy density as high as 0.63 mW h cm<sup>-3</sup> at a high power density of 0.2 W cm<sup>-3</sup>. Thus, the fiber-based flexible SCs show excellent flexibility, great rate capability, and good cycle stability, making these SCs a prospective power source for flexible energy storage devices.

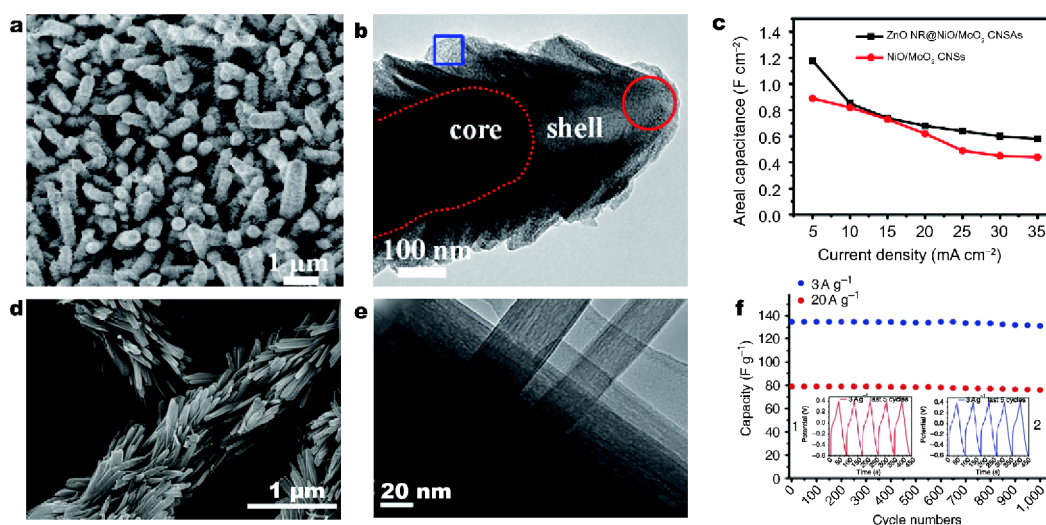
Yu *et al.* [171] fabricated hierarchical graphene/MnO<sub>2</sub> nanostructured sponges by a low-cost “dip and dry”

process with commercial sponges as skeletons. The composite can be operated at a high scan rate of 200 V s<sup>-1</sup> and has superior cycle performance (~90% retention after 10,000 cycles at 10 A g<sup>-1</sup>). As calculated using galvanostatic charge–discharge curves, the highest energy density and power density of sponge@RGO@MnO<sub>2</sub> based device are 8.34 W h kg<sup>-1</sup> and 47 kW kg<sup>-1</sup>, respectively, at an operating voltage of 0.8 V. However, the highest energy density and power density are 2.08 W h kg<sup>-1</sup> and 94 kW kg<sup>-1</sup> for the sponge@RGO under the same condition. The features of low cost, facile preparation, wide operation range, high specific capacitance, high energy and power density, and superior cycling performance could make the as-fabricated SCs as promising devices for commercial production.

Kumar *et al.* [172] reported an interesting work about the fabrication of 3D hierarchical structure composed of 0D Co<sub>3</sub>O<sub>4</sub> nanobeads, 1D carbon nanotubes (CNTs), and 2D graphenes (GNSs) *via* an easy ultrafast microwave irradiation method for high performance supercapacitor electrode. In this unique structure, Co<sub>3</sub>O<sub>4</sub> nanobeads are anchored on CNTs and the CNTs are grown on GNSs, leading to a good electrochemical performance. The electrode possesses a large specific capacitance of 600 F g<sup>-1</sup> at 0.7 A g<sup>-1</sup> (30 wt.% KOH). Furthermore, the electrode also exhibits good cycle stability (94.5% retention after 5,000 cycles at 10 A g<sup>-1</sup>).

Flexible solid-state fiber SCs present the advantages of light weight, high power density, good flexibility, low cost, and environmental friendliness. Zhang *et al.* [173] fabricated a MnO<sub>2</sub>/CFs fiber *via* electrodepositing ultrathin MnO<sub>2</sub> nanosheets on carbon fiber yarns. The specific volumetric and gravimetric capacitances of the single MnO<sub>2</sub>/CFs fiber electrode are calculated to be 58.7 F cm<sup>-3</sup> and 428 F g<sup>-1</sup> based on the mass of MnO<sub>2</sub>. The MnO<sub>2</sub>/CFs electrode demonstrates a large volumetric capacitance because of the synergistic effects of MnO<sub>2</sub> and CFs. The assembled flexible solid-state fiber-like SCs (two MnO<sub>2</sub>/CFs fiber electrodes as anode and cathode, respectively) show a high volumetric energy density (3.8 mW h cm<sup>-3</sup> at a power density of 89 mW cm<sup>-3</sup>), superior flexibility (CV curves are almost unaltered after 2,000 bending times), and an excellent cycling performance (only 14.2% capacitance fade after 10,000 cycles).

By a hydrothermal method, Hu *et al.* [174] fabricated a hierarchical mesoporous NiFe<sub>2</sub>O<sub>4</sub> (NFO) nanocone forest that directly grew on carbon textile (CT). In the NFO–CT sample, the compact bundle of fibers possesses an average diameter of approximately 5 μm. The BET specific surface area of the hierarchical NFO–CT is as



**Figure 11** (a) SEM and (b) TEM images of ZnO NR@NiO/MoO<sub>2</sub> CNSAs; (c) the areal specific capacitances of the two electrodes as a function of current density; (d) SEM image of MnMoO<sub>4</sub>/CoMoO<sub>4</sub> heterostructured nanowires; (e) TEM image at the heterojunction of the hierarchical MnMoO<sub>4</sub>/CoMoO<sub>4</sub> heterostructured nanowires; (f) cycling performance of MnMoO<sub>4</sub>/CoMoO<sub>4</sub> (3D) electrodes tested at 3 and 20 A g<sup>-1</sup> (the inset shows charge-discharge curves cycled at the first and last five cycles at 3 A g<sup>-1</sup>). (a–c) Reproduced with permission from Ref. [176]. Copyright 2014, the American Chemical Society. (d–f) Reproduced with permission from Ref. [177]. Copyright 2011, Nature Publishing Group.

high as 593.60 m<sup>2</sup> g<sup>-1</sup>. As a binder-free electrode, the NFO-CT exhibits specific capacitances of 697, 543.5, 421.8, 355.2, and 303 F g<sup>-1</sup> at 5, 10, 25, 50, and 75 mV s<sup>-1</sup> (6 mol L<sup>-1</sup> LiCl), respectively. Furthermore, the symmetric solid-state SCs device based on NFO-CT demonstrates high capacitance (584 F g<sup>-1</sup> at 5 mV s<sup>-1</sup>) and excellent cycle performance (93.57% capacitance retention after 10,000 cycles). The energy density is calculated to be 54.9 W h kg<sup>-1</sup> at a power density of 300 W kg<sup>-1</sup>. Even at 1372 W kg<sup>-1</sup>, the NFO-CT electrode still achieves an energy density of 25.5 W h kg<sup>-1</sup>, which is substantially higher than those of single/binary metal oxide-based electrodes.

An easy, low-cost, and controllable approach was used by Zhang *et al.* [175] for the synthesis of corrugated NiCo<sub>2</sub>O<sub>4</sub> nanosheets on a nitrogen-doped graphene/carbon nanotube (NGN/CNT) film. The NiCo<sub>2</sub>O<sub>4</sub>/NGN/CNT film electrode possesses a high volumetric capacitance of 482.7 F cm<sup>-3</sup> and a gravimetric capacitance of 2292.7 F g<sup>-1</sup> at 5 A g<sup>-1</sup> (6 mol L<sup>-1</sup> KOH). The electrode also exhibits high rate capability and extremely long-term cycle stability. The asymmetric SCs device was fabricated by using NiCo<sub>2</sub>O<sub>4</sub>/NGN/CNTs as the cathode and NGN/CNTs as the anode. The device exhibits a high gravimetric energy density of 42.71 W h kg<sup>-1</sup> at 775 W kg<sup>-1</sup> and a high gravimetric power density of 15485 W kg<sup>-1</sup> at 24.69 W h kg<sup>-1</sup>. Thus, this material is better than com-

mercially available Ni(OH)<sub>2</sub> used in Ni-MH battery on power density.

#### Other forms of TMOs composites

Via a two-step solution-based approach, Duan *et al.* [176] synthesized a hierarchical core-shell structure of ZnO nanorod@NiO/MoO<sub>2</sub> composite nanosheet arrays (ZnO NR@NiO/MoO<sub>2</sub> CNSAs) on a Ni foam substrate. As shown in Fig. 11a, the ZnO NR@NiO/MoO<sub>2</sub> CNSAs possess a diameter of ~600 nm and length of ~4 μm. The nanorod consists of a ZnO NR “core” and a NiO/MoO<sub>2</sub> CNS “shell”, and the ZnO NRs are well wrapped with ultrathin NiO/MoO<sub>2</sub> CNSs (shown in Fig. 11b). The unique structure favors the penetration of electrolytes into the interior of the active material. The areal specific capacitance of the ZnO NR@NiO/MoO<sub>2</sub> CNSAs is 1.18 F cm<sup>-2</sup> at 5 mA cm<sup>-2</sup> (2 mol L<sup>-1</sup> KOH) (shown in Fig. 11c). Moreover, the material also shows a good cycling performance (only 8.3% loss after 4,000 cycles at 10 mA cm<sup>-2</sup>).

Mai *et al.* [177] synthesized a 3D hierarchical MnMoO<sub>4</sub>/CoMoO<sub>4</sub> heterostructure by a refluxing approach under mild conditions and MnMoO<sub>4</sub> as the backbone material. Fig. 11d shows the morphology and structure of the MnMoO<sub>4</sub>/CoMoO<sub>4</sub> hierarchical heterostructure. The pure MnMoO<sub>4</sub> nanowire backbone materials are approximately 10 μm in length and 500 nm in

diameter. Furthermore, as shown in Fig. 11e, the CoMoO<sub>4</sub> nanorods with diameters of around 50 nm are obtained. The BET specific surface areas of MnMoO<sub>4</sub>, MnMoO<sub>4</sub>/CoMoO<sub>4</sub> nanocomposite, and surface-modified MnMoO<sub>4</sub>/CoMoO<sub>4</sub> are 3.17, 28.0, and 54.06 m<sup>2</sup> g<sup>-1</sup>, respectively. The active sites of the electrode can be adequately accessed due to the larger surface area compared with that in a previous report [178] (15 and 25 m<sup>2</sup> g<sup>-1</sup>, which correspond to MnMoO<sub>4</sub> nanorods and CoMoO<sub>4</sub> nanorods, respectively). The specific capacitances of the hierarchical MnMoO<sub>4</sub>/CoMoO<sub>4</sub> heterostructured nanowires is 187.1 F g<sup>-1</sup> at 1 A g<sup>-1</sup> (2 mol L<sup>-1</sup> NaOH), which is evidently higher than those of pure 1D nanorod MnMoO<sub>4</sub> (9.7 F g<sup>-1</sup>), CoMoO<sub>4</sub> (62.8 F g<sup>-1</sup>), and the MnMoO<sub>4</sub>/CoMoO<sub>4</sub> nanocomposite (69.2 F g<sup>-1</sup>). Fig. 11f displays excellent reversibility of the hierarchical MnMoO<sub>4</sub>/CoMoO<sub>4</sub> electrode with high cycling efficiency of up to 98% after 1,000 cycles.

Through a stepwise hydrothermal method, Mai *et al.* [179] designed and synthesized 3D self-supported Co<sub>3</sub>O<sub>4</sub>@CoMoO<sub>4</sub> core-shell architectures that directly grew on Ni foam. The Co<sub>3</sub>O<sub>4</sub>@CoMoO<sub>4</sub> shows a high capacitance of 1902 F g<sup>-1</sup> at 1 A g<sup>-1</sup> and good cycling stability with 1% capacitance loss after 5,000 cycles at 5 A g<sup>-1</sup> (2 mol L<sup>-1</sup> KOH). The asymmetric SCs device was fabricated by using Co<sub>3</sub>O<sub>4</sub>@CoMoO<sub>4</sub> as the cathode and the CNTs on Ni foam as the anode. The device delivers a high energy density of 45.2 W h kg<sup>-1</sup> at a power density of 400 W kg<sup>-1</sup> and good cycling performance (capacitance retention of 98.5% after 3,000 cycles at 0.5 A g<sup>-1</sup>). The good electrochemical performance of Co<sub>3</sub>O<sub>4</sub>@CoMoO<sub>4</sub> is ascribed to the unique architecture with a large interfacial area and numerous channels for the rapid diffusion of electrolyte ions.

High areal specific capacitance per area is of great importance for the practical application of supercapacitors. To realize this goal, it need to combine high mass-loading of the active material and high utilization ratio of the material. Sun *et al.* [180] prepared a ternary hierarchical core-shell structure of Co<sub>3</sub>O<sub>4</sub>@Ni-Co-O arrays *via* an easy and cost-effective strategy (Fig. 12a-c). As shown in Fig. 12a, the Co<sub>3</sub>O<sub>4</sub> microsheet grown on foam Ni substrate is the core, and the aligned slim Ni-Co-O nanorods (diameter <20 nm) are coated on it. This structure exhibits an excellent electrochemical performance when utilized as a supercapacitor electrode. The electrode with a high areal mass-loading of 12 mg cm<sup>-2</sup> possesses a high specific capacitance of 2098 F g<sup>-1</sup> at 5 mA cm<sup>-2</sup> (1 mol L<sup>-1</sup> KOH) (Fig. 12d). Furthermore, Sun *et al.* [181] also fabricated a hierarchical core-shell

structure of Co<sub>3</sub>O<sub>4</sub>@NiO nanowire@nanorod arrays *via* a similar strategy (Fig. 12e). The NiO nanorods were *in-situ* grown on the surface of Co<sub>3</sub>O<sub>4</sub> nanowire arrays grown on foam Ni substrate (Fig. 12f-i). The electrode with a high mass-loading of 19.5 mg cm<sup>-1</sup> delivers a high specific capacitance of 2033 F g<sup>-1</sup> at 5 mA cm<sup>-2</sup> (1 mol L<sup>-1</sup> KOH). The areal capacitance is up to 39.6 F cm<sup>-2</sup>, which is much higher than that of pure Co<sub>3</sub>O<sub>4</sub> electrode (6.7 F cm<sup>-2</sup>) (Fig. 12j, k). The excellent performance of these core-shell structure arrays is mainly attributed to the special hierarchical structure and the synergistic effect of different components. Based on the above two works, Sun *et al.* [182] further prepared hierarchical Co<sub>x</sub>Fe<sub>3-x</sub>O<sub>4</sub> arrays directly grown on Cu foam. Combining the above hierarchical Co<sub>3</sub>O<sub>4</sub>@Ni-Co-O arrays as the cathode, an aqueous battery was assembled. The battery shows an energy density of ~2.08 mW h cm<sup>-2</sup> at a power density of ~4.89 mW cm<sup>-2</sup>, and an energy density of ~1.36 mW h cm<sup>-2</sup> at a power density of ~42.56 mW cm<sup>-2</sup> (6 mol L<sup>-1</sup> KOH). This indicates that hierarchically nanostructured metal oxides also have potential applications in the field of aqueous battery [182].

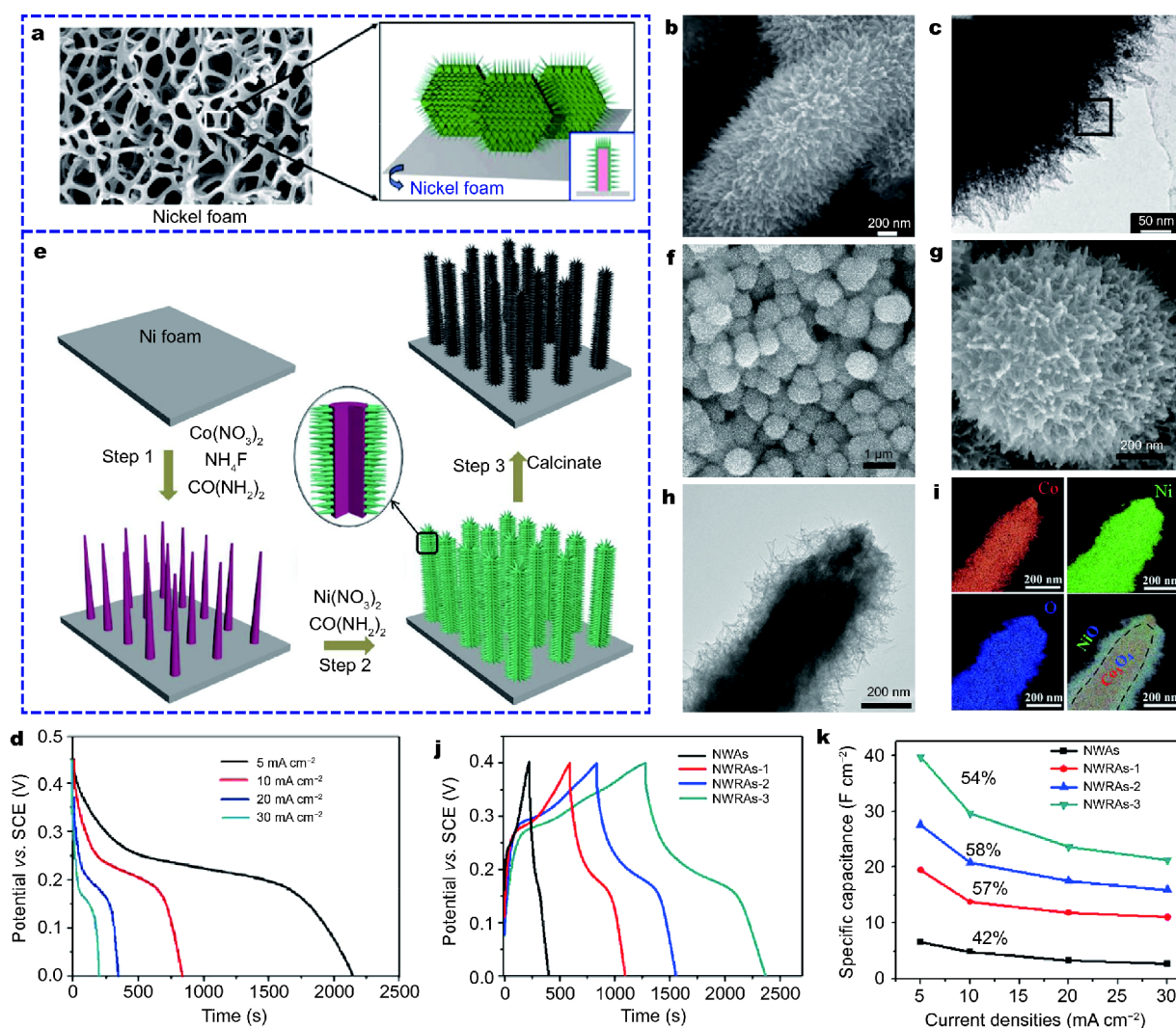
Iron oxides have been considered to be promising anode materials for supercapacitors due to their low cost, abundance, non-toxicity, and functionality in negative potentials [183-185]. Recently, Lin and co-workers [183] prepared a hierarchical Fe<sub>2</sub>O<sub>3</sub> nanotube array directly grown on Ni foam *via* chemical transformation of ZnO nanowire. The characterization results show that the walls of nanotube are mainly composed of α-Fe<sub>2</sub>O<sub>3</sub> nanoparticles mixed with a small quantity of ZnO nanoparticles. The electrochemical test results indicate that the hierarchical structure electrode exhibits a high reversible capacitance of 300.1 F g<sup>-1</sup> at 0.75 A g<sup>-1</sup> (1 mol L<sup>-1</sup> Li<sub>2</sub>SO<sub>4</sub>).

A comparison of typical hierarchically nanostructured TMOs for SCs is given in Table 1. The morphologies and structures of TMOs are important influential factors for the corresponding electrochemical performance. Moreover, the performance of the reported asymmetric supercapacitors is summarized in Table 2.

## CONCLUSIONS AND OUTLOOKS

In this review, we summarized the recent progress in the field of hierarchically nanostructured TMOs for SCs. Hierarchically nanostructured TMOs with various structures and compositions have been fabricated *via* different synthesis methods. The primary structure mainly includes spheres, hollow spheres, rods, and tubes at micrometer scale or sub-micrometer scale. The secondary structure is mainly a 2D nanosheet, which is not only





**Figure 12** (a) Schematic image for the design of hierarchical core-shell  $\text{Co}_3\text{O}_4@Ni-Co-O$  nanoarray (the  $\text{Co}_3\text{O}_4$  nanosheet is shown in pink and the  $Ni-Co-O$  nanorod is shown in green); (b, c) SEM and TEM images of the hierarchical  $\text{Co}_3\text{O}_4@Ni-Co-O$  arrays; (d) galvanostatic discharge curves of the hierarchical  $\text{Co}_3\text{O}_4@Ni-Co-O$  arrays at various current densities; (e) schematic image for the design of hierarchical core-shell  $\text{Co}_3\text{O}_4@NiO$  arrays (in this work, three samples were fabricated by adding 1, 2, and 3 mmol  $Ni(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  during the synthesis process. These three samples were denoted as NWRAs-1, NWRAs-2, and NWRAs-3, respectively.  $\text{Co}_3\text{O}_4$  nanowire arrays sample was denoted as NWAs); (f, g) SEM images of NWRAs-3 at different magnifications; (h, i) TEM and EDS mapping images of NWRAs-3; (j) galvanostatic charge and discharge curves at  $10 \text{ mA cm}^{-2}$ ; (k) plots of areal specific capacitance versus current density. (a–d) Reproduced with permission from Ref. [180]. Copyright 2012, Springer. (e–k) Reproduced with permission from Ref. [181]. Copyright 2014, Elsevier.

beneficial to the stability of the hierarchical structure but also conducive to electrochemical reaction. Single-metal oxides, bimetallic oxides, the composites of different metal oxides, and the composites of metal oxides with carbon nanomaterials or noble metal NPs have been studied extensively for the compositions of hierarchically nanostructured TMOs. In general, bimetallic oxides or composites with different metal oxides exhibit higher electrochemical activities compared with single-metal oxides because of the complex chemical compositions

and the synergetic effect of the individual components.

For further improvement in the performance of SCs, the development of new types of hierarchically nanostructured TMO materials would become the focus of future research. The details can be listed as follows:

(1) The incorporation of TMO materials with various nanostructured carbon materials, such as CNTs, CFs, and graphene, can not only inherit the 1D or 2D structures of these carbon materials but also can effectively improve the electrical conductivity of the TMOs. The synthesized

**Table 1** Comparison of typical hierarchically nanostructured TMOs as electrodes of SCs in three-electrode systems

Materials	SSA <sup>a</sup> (m <sup>2</sup> g <sup>-1</sup> )	Electrolyte	Capacitance/current density	Retention (%) / cycles / current density	Ref.
Flower-like α-MnO <sub>2</sub>	216	1 mol L <sup>-1</sup> K <sub>2</sub> SO <sub>4</sub>	298 F g <sup>-1</sup> / 0.117 A g <sup>-1</sup>	90/2000/2 A g <sup>-1</sup>	[76]
α-MnO <sub>2</sub> microspheres	/	1 mol L <sup>-1</sup> Na <sub>2</sub> SO <sub>4</sub>	365 F g <sup>-1</sup> / 2 A g <sup>-1</sup>	100/2000/2 A g <sup>-1</sup>	[77]
β-MnO <sub>2</sub> nanoflowers	267	1 mol L <sup>-1</sup> Na <sub>2</sub> SO <sub>4</sub>	296.3 F g <sup>-1</sup> / 2 mV s <sup>-1</sup>	/	[78]
MnO <sub>2</sub> NFs <sup>b</sup>	269	1 mol L <sup>-1</sup> Na <sub>2</sub> SO <sub>4</sub>	176 F g <sup>-1</sup> / 20 A g <sup>-1</sup>	100/2000/2 A g <sup>-1</sup>	[79]
δ-MnO <sub>2</sub> microspheres	238	1 mol L <sup>-1</sup> Na <sub>2</sub> SO <sub>4</sub>	364 F g <sup>-1</sup> / 1 A g <sup>-1</sup>	100/6000/10 A g <sup>-1</sup>	[80]
Co <sub>3</sub> O <sub>4</sub> film	/	2 mol L <sup>-1</sup> KOH	352 F g <sup>-1</sup> / 2 A g <sup>-1</sup>	/	[91]
Enoki mushroom-like Co <sub>3</sub> O <sub>4</sub>	/	6 mol L <sup>-1</sup> KOH	787 F g <sup>-1</sup> / 1 A g <sup>-1</sup>	94.5/1000/10 A g <sup>-1</sup>	[92]
HFC Co <sub>3</sub> O <sub>4</sub> <sup>c</sup>	245.5	2 mol L <sup>-1</sup> KOH	948.9 F g <sup>-1</sup> / 1 A g <sup>-1</sup>	/	[93]
NiO NWs <sup>d</sup>	/	6 mol L <sup>-1</sup> KOH	1493 F g <sup>-1</sup> / 3 A g <sup>-1</sup>	87/2000/50 mV s <sup>-1</sup>	[100]
NiO NTAs <sup>e</sup>	165	1 mol L <sup>-1</sup> Na <sub>2</sub> SO <sub>4</sub>	675 F g <sup>-1</sup> / 2 A g <sup>-1</sup>	93.2/10000/2 A g <sup>-1</sup>	[101]
D-NiO <sup>f</sup>	92.99	2 mol L <sup>-1</sup> KOH	612.5 F g <sup>-1</sup> / 0.5 A g <sup>-1</sup>	90/1000/0.5 A g <sup>-1</sup>	[102]
NiO-HMNAs <sup>g</sup>	312.6	2 mol L <sup>-1</sup> KOH	3114 F g <sup>-1</sup> / 5 mA cm <sup>-2</sup>	87.6/4000/30 mA cm <sup>-2</sup>	[103]
CNRNP <sup>h</sup>	/	3 mol L <sup>-1</sup> KOH	800 F g <sup>-1</sup> / 200 mV s <sup>-1</sup>	/	[106]
Flower-like CuO	/	5 mol L <sup>-1</sup> NaOH	1641 mF cm <sup>-2</sup> / 2 mA cm <sup>-2</sup>	79/10000/4 mA cm <sup>-2</sup>	[107]
Flower-shaped CuO	119.6	1 mol L <sup>-1</sup> KOH	520 F g <sup>-1</sup> / 1 A g <sup>-1</sup>	95.2/5000/1 A g <sup>-1</sup>	[108]
Bi <sub>2</sub> O <sub>3</sub> NBs <sup>i</sup>	196	1 mol L <sup>-1</sup> Na <sub>2</sub> SO <sub>4</sub>	250 F g <sup>-1</sup> / 100 mV s <sup>-1</sup>	100/1000/100 mV s <sup>-1</sup>	[113]
Rod-like Bi <sub>2</sub> O <sub>3</sub>	/	6 mol L <sup>-1</sup> KOH	1350 F g <sup>-1</sup> / 0.1 A g <sup>-1</sup>	97.6/1000/0.1 A g <sup>-1</sup>	[114]
NiCo <sub>2</sub> O <sub>4</sub> microspheres	148.5	6 mol L <sup>-1</sup> KOH	1006 F g <sup>-1</sup> / 1 A g <sup>-1</sup>	93.2/1000/8 A g <sup>-1</sup>	[124]
NiCo <sub>2</sub> O <sub>4</sub> MHSs <sup>j</sup>	118.3	3 mol L <sup>-1</sup> KOH	2623 F g <sup>-1</sup> / 1 A g <sup>-1</sup>	99.2/3000/10 A g <sup>-1</sup>	[125]
NiCoO <sub>2</sub> NTs <sup>k</sup>	98.9	2 mol L <sup>-1</sup> KOH	1468 F g <sup>-1</sup> / 2 A g <sup>-1</sup>	99.2/3000/10 A g <sup>-1</sup>	[126]
ZnV <sub>2</sub> O <sub>4</sub> NHNs <sup>l</sup>	/	2 mol L <sup>-1</sup> KOH	385 F g <sup>-1</sup> / 0.5 A g <sup>-1</sup>	89/1000/1 A g <sup>-1</sup>	[127]
CoO@MnO <sub>2</sub> core-shell	154.95	6 mol L <sup>-1</sup> KOH	1835 F g <sup>-1</sup> / 1 A g <sup>-1</sup>	97.7/10000/1 A g <sup>-1</sup>	[136]
Fe <sub>3</sub> O <sub>4</sub> -MnO <sub>2</sub> microspheres	/	1 mol L <sup>-1</sup> Na <sub>2</sub> SO <sub>4</sub>	367.4 F g <sup>-1</sup> / 100 mV s <sup>-1</sup>	76/5000/5 A g <sup>-1</sup>	[137]
Co <sub>3</sub> O <sub>4</sub> @MnO <sub>2</sub> NAs <sup>m</sup>	/	1 mol L <sup>-1</sup> LiOH	1905.4 F g <sup>-1</sup> / 0.5 A g <sup>-1</sup>	89.8/5000/2 A g <sup>-1</sup>	[138]
Cu <sub>0.27</sub> Co <sub>2.73</sub> O <sub>4</sub> /MnO <sub>2</sub> NRAs <sup>n</sup>	/	6 mol L <sup>-1</sup> KOH	3.1 F cm <sup>-2</sup> / 24.8 mA cm <sup>-2</sup>	/	[139]
NiCo <sub>2</sub> O <sub>4</sub> @MnO <sub>2</sub> core-shell	75.06	1 mol L <sup>-1</sup> NaOH	1595.1 F g <sup>-1</sup> / 3 mA cm <sup>-2</sup>	92.6/2000/40 mA cm <sup>-2</sup>	[140]
NiCo <sub>2</sub> O <sub>4</sub> @MnO <sub>2</sub> nanosheets	/	1 mol L <sup>-1</sup> KOH	913.6 F g <sup>-1</sup> / 0.5 A g <sup>-1</sup>	87.1/3000/0.5 A g <sup>-1</sup>	[141]
Dumbbell-like Au-Fe <sub>3</sub> O <sub>4</sub>	/	1 mol L <sup>-1</sup> KOH	464 F g <sup>-1</sup> / 1 A g <sup>-1</sup>	86.4/1000/10 A g <sup>-1</sup>	[146]
Co <sub>3</sub> O <sub>4</sub> @Au@MnO <sub>2</sub> (NSs)HHS <sup>o</sup>	/	1 mol L <sup>-1</sup> LiOH	1532.4 F g <sup>-1</sup> / 1 A g <sup>-1</sup>	115/5000/10 A g <sup>-1</sup>	[147]
ZnO@Au@NiO	/	1 mol L <sup>-1</sup> KOH	3.5 F cm <sup>-2</sup> / 2 mA cm <sup>-2</sup>	80.3/4000/30 mA cm <sup>-2</sup>	[151]
MnO <sub>2</sub> /RGO/CF <sup>p</sup>	/	1 mol L <sup>-1</sup> Na <sub>2</sub> SO <sub>4</sub>	13.7 F cm <sup>-3</sup> / 0.5 mA cm <sup>-2</sup>	/	[170]
3D Co <sub>3</sub> O <sub>4</sub> -nb@CG <sup>q</sup>	/	30 wt.% KOH	600.19 F g <sup>-1</sup> / 0.7 A g <sup>-1</sup>	95.4/5000/1.1 A g <sup>-1</sup>	[172]
NiFe <sub>2</sub> O <sub>4</sub> -CT <sup>r</sup>	/	6 mol L <sup>-1</sup> LiCl	697 F g <sup>-1</sup> / 5 mV s <sup>-1</sup>	/	[174]
NiCo <sub>2</sub> O <sub>4</sub> /NGN/CNTs <sup>s</sup>	/	6 mol L <sup>-1</sup> KOH	2292.7 F g <sup>-1</sup> / 5 A g <sup>-1</sup>	125/10000/30 A g <sup>-1</sup>	[175]
ZnO NR@NiO/MoO <sub>2</sub> CNSAs <sup>t</sup>	/	2 mol L <sup>-1</sup> KOH	1.18 F cm <sup>-2</sup> / 5 mA cm <sup>-2</sup>	91.7/4000/10 mA cm <sup>-2</sup>	[176]
MnMoO <sub>4</sub> /CoMoO <sub>4</sub> nanowires	54.06	2 mol L <sup>-1</sup> NaOH	187.1 F g <sup>-1</sup> / 1 A g <sup>-1</sup>	98/1000/20 A g <sup>-1</sup>	[177]
Co <sub>3</sub> O <sub>4</sub> @CoMoO <sub>4</sub> core-shell	61.4	2 mol L <sup>-1</sup> KOH	1902 F g <sup>-1</sup> / 1 A g <sup>-1</sup>	99/5000/5 A g <sup>-1</sup>	[179]
Co <sub>3</sub> O <sub>4</sub> @Ni-Co-O NSRAs <sup>u</sup>	31.1	1 mol L <sup>-1</sup> KOH	2098 F g <sup>-1</sup> / 5 mA cm <sup>-2</sup>	96/1000/30 mA cm <sup>-2</sup>	[180]
Co <sub>3</sub> O <sub>4</sub> @NiO NWRAs <sup>v</sup>	116	1 mol L <sup>-1</sup> KOH	2033 F g <sup>-1</sup> / 5 mA cm <sup>-2</sup>	100/1000/30 mA cm <sup>-2</sup>	[181]
α-Fe <sub>2</sub> O <sub>3</sub> nanotubes	/	1 mol L <sup>-1</sup> Li <sub>2</sub> SO <sub>4</sub>	300.1 F g <sup>-1</sup> / 0.75 A g <sup>-1</sup>	/	[183]

a) SSA: specific surface area. b) MnO<sub>2</sub> NFs: MnO<sub>2</sub> nanoflakes; c) HFC Co<sub>3</sub>O<sub>4</sub>: hollow fluffy cages Co<sub>3</sub>O<sub>4</sub>; d) NiO NWs: NiO nanowires; e) NiO NTAs: NiO nanotube arrays; f) D-NiO: double-shelled NiO; g) NiO-HMNAs: hierarchical mesoporous NiO nanoarrays; h) CNRNP: CuO nanoribbon-on-Ni-nanoporous/Ni foam; i) Bi<sub>2</sub>O<sub>3</sub> NBs: Bi<sub>2</sub>O<sub>3</sub> nanobelts; j) NiCo<sub>2</sub>O<sub>4</sub> MHSs: NiCo<sub>2</sub>O<sub>4</sub> multiple hierarchical structures; k) NiCoO<sub>2</sub> NTs: NiCoO<sub>2</sub> nanotube; l) ZnV<sub>2</sub>O<sub>4</sub> NHNs: ZnV<sub>2</sub>O<sub>4</sub> novel hierarchical nanospheres; m) Co<sub>3</sub>O<sub>4</sub>@MnO<sub>2</sub> NAs: Co<sub>3</sub>O<sub>4</sub>@MnO<sub>2</sub> nanoneedle arrays; n) Cu<sub>0.27</sub>Co<sub>2.73</sub>O<sub>4</sub>/MnO<sub>2</sub> NRAs: Cu<sub>0.27</sub>Co<sub>2.73</sub>O<sub>4</sub>/MnO<sub>2</sub> nanorod arrays; o) Co<sub>3</sub>O<sub>4</sub>@Au@MnO<sub>2</sub> (NSs) HHS: Co<sub>3</sub>O<sub>4</sub>@Au@MnO<sub>2</sub> nanosheet hierarchical heterostructures; p) MnO<sub>2</sub>/RGO/CF: MnO<sub>2</sub>/reduced graphene oxide/carbon nanofiber; q) Co<sub>3</sub>O<sub>4</sub>-nb@CG: Co<sub>3</sub>O<sub>4</sub> nanobeads-CNTs (carbon nanotubes)-GNSs (graphene nanosheets). r) NiFe<sub>2</sub>O<sub>4</sub>-CT: NiFe<sub>2</sub>O<sub>4</sub> nanocone forest on carbon textile; s) NiCo<sub>2</sub>O<sub>4</sub>/NGN/CNTs: NiCo<sub>2</sub>O<sub>4</sub> nanosheets on nitrogen-doped graphene/carbon nanotubes; t) ZnO NR@NiO/MoO<sub>2</sub> CNSAs: ZnO nanorod@NiO/MoO<sub>2</sub> composite nanosheet arrays; u) Co<sub>3</sub>O<sub>4</sub>@Ni-Co-O NSRAs: Co<sub>3</sub>O<sub>4</sub>@Ni-Co-O nanosheet@nanorod arrays; v) Co<sub>3</sub>O<sub>4</sub>@NiO NWRAs: Co<sub>3</sub>O<sub>4</sub>@NiO nanowire@nanorod arrays.

**Table 2** Typical hierarchically nanostructured TMOs as cathodes of asymmetric SCs

Cathode materials	Anode materials	Working voltage	Device performance <sup>a</sup>		Ref.
			Energy density	Power density	
$\delta$ -MnO <sub>2</sub> microspheres	Activated carbon	0–2 V	48.06 W h kg <sup>-1</sup>	1.0 kW kg <sup>-1</sup>	[80]
Enoki mushroom-like Co <sub>3</sub> O <sub>4</sub>	Carbon	0–1.5 V	23.9 W h kg <sup>-1</sup>	0.375 kW kg <sup>-1</sup>	[92]
CoO@MnO <sub>2</sub> core-shell	Nitrogen-doped graphene	0–1.8 V	85.9 W h kg <sup>-1</sup>	852.4 W kg <sup>-1</sup>	[136]
NiCo <sub>2</sub> O <sub>4</sub> @MnO <sub>2</sub> nanosheets	Activated carbon	0–1.5 V	37.5 W h kg <sup>-1</sup>	187.5 W kg <sup>-1</sup>	[141]
MnO <sub>2</sub> /RGO/CF <sup>b</sup>	GH/CW <sup>c</sup>	0–1.6 V	0.63 mW h cm <sup>-3</sup>	0.2 W cm <sup>-3</sup>	[170]
NiCo <sub>2</sub> O <sub>4</sub> /NGN/CNTs <sup>d</sup>	NGN/CNTs <sup>e</sup>	0–1.55 V	42.7 W h kg <sup>-1</sup>	775 W kg <sup>-1</sup>	[175]
Co <sub>3</sub> O <sub>4</sub> @CoMoO <sub>4</sub> core-shell	CNTs <sup>f</sup>	0–1.6 V	45.2 W h kg <sup>-1</sup>	400 W kg <sup>-1</sup>	[179]

a) Device performance: the energy density of the asymmetric SCs device under a certain power density. b) MnO<sub>2</sub>/RGO/CF: MnO<sub>2</sub>/reduced graphene oxide/carbon nanofiber; c) GH/CW: graphene hydrogel-wrapped Cu wire; d) NiCo<sub>2</sub>O<sub>4</sub>/NGN/CNTs: NiCo<sub>2</sub>O<sub>4</sub> nanosheets on nitrogen-doped graphene/carbon nanotubes; e) NGN/CNTs: nitrogen-doped graphene/carbon nanotubes; f) CNTs: carbon nanotubes.

multi-component composites can maximize the benefits from all components, thereby making this approach a highly effective method to improve the performance of the TMO materials. Despite several reports on the composites of metal oxides with carbon nanomaterials, these materials still present massive development space in the future.

(2) Compared with general nanostructured TMOs, hierarchically nanostructured TMOs exhibits higher specific capacitance and better rate performance. However, although the hierarchical nanostructure is favorable for the electrochemical reaction of TMO electrode materials, this special structure often leads to the low tap density of the materials. Therefore, new reasonable structures should be designed for hierarchically nanostructured TMOs to endure large volume energy densities.

(3) It is obvious that the specific capacitances of most of the cobalt-based materials and nickel-based materials are much larger than those of other materials. Therefore, these materials are promising for practical applications. The future research of TMOs-based electrode materials can be focused on cobalt-based materials and nickel-based materials.

(4) The asymmetric SCs are a hot spot in the SC field at present. For asymmetric SCs, various negative and positive electrode materials with well-separated potential windows can be combined to maximize the output voltage; thus, the specific energy of SCs will be markedly increased.

(5) The self-supporting flexible electrode in SCs is another important research direction. When self-supporting flexible materials are used as electrodes, the conductive carbon and bonding agent are unnecessary for the assembly of SC device; thus, the energy density of device can be effectively improved. In addition, the self-supporting flexible electrode can enhance the circulation

stability of device. Furthermore, the flexible all-solid-state asymmetric SCs device is crucial because of several advantageous properties, such as a wide operating voltage range, high energy densities, excellent flexibility, and superior long term cycling stability.

(6) Aqueous rechargeable batteries, such as Ni–Zn battery, Ni–MH battery, and Ni–Fe battery, have attracted renewed interest because of their high theoretical energy density, long cycling life, low cost, and safety [186]. Hierarchically nanostructured TMOs reviewed in this paper also can be applied in aqueous batteries [186]. This is also a very important research direction.

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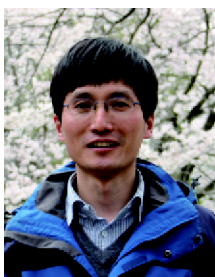
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**Conflict of interest** The authors declare that they have no conflict of interest.



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## 多级纳米结构过渡金属氧化物作为超级电容器电极材料的应用

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**摘要** 为了应对化石燃料短缺与日益严重的环境污染问题, 开发高效、清洁、可持续的电化学储能技术已迫在眉睫. 超级电容器, 由于其功率密度高、充放电时间短、循环寿命长等特点, 已得到广泛关注. 多种过渡金属氧化物已被作为超级电容器电极材料进行了深入研究. 为了进一步提高性能, 具有多级纳米结构的过渡金属氧化物材料已成为目前超级电容器领域的研究热点. 多级纳米结构不仅可以为电化学反应提供更多活性位点, 同时还可以缩短离子的传输路径. 本综述对多级纳米结构过渡金属氧化物在超级电容器电极材料方面的应用, 进行了系统的总结与评价, 主要包括: 合成方法、成分、结构和电化学性能. 此外, 对该领域的进一步发展进行了展望.