Hierarchical MCo$_2$O$_4$@Ni(OH)$_2$ ($M = \text{Zn or Mn}$) core@shell architectures as electrode materials for asymmetric solid-state supercapacitors

Erdenebayar Baasanjav$^a$, Parthasarathi Bandyopadhyay$^{a,*}$, Jung Sang Cho$^{b,*}$, Sang Mun Jeong$^{b,*}$

$^a$ Department of Chemical Engineering, Chungbuk National University, 1 Chungdae-ro, Seowon-Gu, Cheongju, Chungbuk 28644, Republic of Korea
$^b$ Department of Engineering Chemistry, Chungbuk National University, 1 Chungdae-ro, Seowon-Gu, Cheongju, Chungbuk 28644, Republic of Korea

ARTICLE INFO
Keywords:
Hierarchical Core@shell Nitrogen-doped carbon Solid-state supercapacitor Energy density

ABSTRACT
In this study, the self-assembled Ni(OH)$_2$-nanosheet-adorned hierarchical MCo$_2$O$_4$@Ni(OH)$_2$ ($M = \text{Zn or Mn}$) core@shell heterostructures are prepared by a three-step process, via tuning the core-compositions, as advanced electrodes for supercapacitors (SCs). The tuning of the core composition makes a significant impact on the physicochemical properties, morphology, and electrochemical performance. Among the MCo$_2$O$_4$@Ni(OH)$_2$ materials, the nanopine forest-like ZnCo$_2$O$_4$@Ni(OH)$_2$ optimal architecture exhibits superior supercapacitive performance (areal-specific capacity, 1.34 mAh cm$^{-2}$/432.6 mAh g$^{-1}$ at 3 mA cm$^{-2}$ current density and a ~90% cycling stability upto 5000 cycles). Meanwhile, 3D porous nitrogen-doped carbon (PNC) with perfect rhombic dodecahedral morphology is used as negative electrode material with high surface area (1600 m$^2$ g$^{-1}$), excellent capacity (49.2 mAh g$^{-1}$ at 2 mA cm$^{-2}$) and rate performance (~55% at 50 mA cm$^{-2}$). The solid-state asymmetric device comprising ZnCo$_2$O$_4$@Ni(OH)$_2$ (positive electrode) and hierarchical PNC (negative electrode) affords a high cell capacity of 97.8 mAh g$^{-1}$ at 4 mA cm$^{-2}$, with 86% cycle stability after 10,000 cycles. Moreover, the device exhibits 78.2 W h kg$^{-1}$ of energy density at a power density of 451 W kg$^{-1}$ and 40.4 W h kg$^{-1}$ of energy density at 4691.0 W kg$^{-1}$ of power density. This study provides insight into electro-active material design and construction of heteronanostructures for high-performance SCs.

1. Introduction

Supercapacitors (SCs) are promising electrochemical energy storage devices that join the gap between traditional capacitors and rechargeable batteries [1,2]. Owing to their low production cost, high charging-discharging efficiency, excellent power density, long cycling lifetime, and environmental benignity, SCs are suitable for a wide range of applications, such as hybrid electrical vehicles, portable electronic materials, and smart electricity grids [3–7]. Current research has concentrated on designing and fabricating advanced SCs that can store a large quantity of energy within a short time. Pseudocapacitive (battery-type) electrode materials are extensively considered as positive electrode materials for SCs. This is because their typical fast redox reactions lead to higher specific capacities and energy densities than those of carbonaceous electrode materials based on the electrochemical double-layer charge-storage reaction mechanism [2,8].

Among the various pseudocapacitive materials, multicomponent transitional metal oxides (TMOs)/hydroxides (TMOHs) are preferentially utilized as electrode material for SCs because of their multiple chemical valence states, structural/morphological flexibility, good electrochemical activity, and low production cost [9–14]. The cobalt-based binary oxides (MnCo$_2$O$_4$ and ZnCo$_2$O$_4$) have shown superior electrochemical activity to that of their unitary metal oxide analogues [8,15–17]. However, the voltage window, recharging ability, rate capability, and cycle life of binary TMOs are still mediocre for practical application. Indeed, the foremost challenge of employing binary TMOs as electrode materials for SCs is how to further boost their electrochemical outcome for application in advanced energy-storage devices. An excellent method to resolve these shortfalls is to rationally design and construct multicomponent hybrid complex assemblies using binary TMO-based nanostructures with other pseudocapacitive TMOs/TMOHs on a conductive substrate [8]. Among the different TMOHs, layered nickel hydroxide [Ni(OH)$_2$] is a desirable pseudocapacitive candidate for SCs, owing to its high theoretical capacity, excellent electrochemical
redox activity, environmental benignity, and availability in different morphologies [17–19]. However, its electrical conductivity, rate performance, and cycling stability are generally unsatisfactory [20–22]. The construction of hierarchical core@shell heterostructures consisting of conductive TMOs as the core (conductive scaffolds/secondary substrate) and Ni(OH)2 as the shell layer is a unique approach to overcome the limitations of individual materials and fully utilize their advantages. Hybrid hierarchical heterostructures prepared from binary TMOs and Ni(OH)2 have already been reported. Zhao et al. created MnCo2O4@Ni(OH)2 hybrid hierarchical heterostructures prepared from binary TMOs and Ni(OH)2, which delivered a C∞ retention up to 20 A g−1 and a rate performance of 32.6% at 20 A g−1 [8]. Liu et al. synthesized MnCo2O4@Ni(OH)2, a flower-like electrode that exhibited a C∞ value of 2544.44 F g−1 at 3 A g−1 and 82.8% rate performance up to 20 A g−1, with 87.7% cyclic stability after 5000 cycles [17]. Wu et al. synthesized a hierarchical CoO@Ni(OH)2 nanostructure electrode that exhibited a C∞ of 1418.2 F g−1 at 1 A g−1 and a rate capability of 65% at 10 A g−1, with a cycle stability of 93.7% after 5000 consecutive cycles [19]. Li et al. developed CoO@Ni(OH)2 material onto Ni-modified surfaces and channels of a well-ordered macroporous silicon electrode plate for SCs [20]. The electrode showed a C∞ value of 1812.42 F g−1 at 2 mA cm−2 and a rate performance of 45.9% at 32 mA cm−2, with a lifespan of 87.42% after 5000 cycles. Zhu et al. synthesized carbon cloth-supported CuCo2O4@Ni(OH)2 hybrid material as a positive electrode for SCs, which delivered a C∞ of 2160 F g−1 at 1 A g−1, 82.7% capacitance retention up to 20 A g−1, and 92% cyclic stability up to 5000 cycles [18]. However, the above TMO@Ni(OH)2 core@shell materials cannot fulfill the requirements for superior energy storage devices. To date, the construction of hierarchical core@shell heterostructures consisting of conductive TMOs as the core (conductive scaffolds/secondary substrate) and Ni(OH)2 as the shell layer is a crucial challenge. The hetero-growth of mixed TMO- and TMOH-based core@shell structures is challenging to control because of their apparent structural diversity, which results in improper morphology and structure and poor electrochemical properties. More importantly, the above-mentioned literature survey clearly illustrates that although the shell was based on Ni(OH)2 in each core@shell material, the synthetic method of the Ni(OH)2 shell preparation was different in each case. Therefore, the assimilation of Ni(OH)2 shell onto different TMO core materials with different structural features, for SC application through a similar synthetic protocol, is highly desirable.

With these facts in mind, in this study, we rationally designed and successfully fabricated hierarchical MCo2O4@Ni(OH)2 (M = Zn or Mn) core@shell architectures on Ni-foam (NF) by varying the composition of core materials (MCo2O4) via similar experimental condition. The primary objectives and merits of the present study are as follows: (i) The assembly of a core@shell structure consisting of different core compositions and a fixed shell is valuable in realizing the required electrochemical storage performance based on structural and morphological features. The hierarchical conductive MCo2O4 (M = Zn or Mn) nanowire arrays (NWs) grown directly on conductive NF act as the backbone and “electronic superhighway medium” for charge transport and storage, overcoming the low conductivity of the shell [19]. In this context, the selection of a suitable bimetallic oxide core can enable to boost the electrochemical performance. (ii) The thickness of the shell material strongly influences the supercapacitive performance of the core@shell [23]. Therefore, the thickness of the Ni(OH)2 nanosheets was tuned by changing the hydrothermal shell growth reaction times to obtain optimum electrochemical performance. (iii) The hierarchical core@shell materials are grown directly onto the 3D NF, which enhances the electrical conductivity and also helps to reduce the ion-diffusion path length at the electrode/electrolyte interface.

Among the prepared MCo2O4@Ni(OH)2 materials, ZnCo2O4@Ni(OH)2 exhibited the finest morphology, highest specific surface area (SA), and superior electrochemical performance. Thus, the ZnCo2O4@Ni(OH)2 NW array as positive electrode was then used to assemble an asymmetric SC (ASC) device, in which KOH/PVA and the 3D ZIF-8-derived porous nitrogen-based carbon (PNC) served as the gel-electrolyte and negative electrode material, respectively. The asymmetric solid-state device exhibited an outstanding combination of energy and power densities together with a long cycle life.

2. Experimental section

2.1. Synthesis of M-Co-oxide nanowire arrays (MCo2O4 NWs; M = Zn or Mn)

The NFs were cleaned thoroughly according to our reported literature [3,5]. The MCo2O4 NWs on the NF substrate were grown by an easy hydrothermal reaction method followed by calcination. In brief, an aqueous precursor solution of Co(NO3)2·6H2O (0.291 g), Zn(NO3)2·6H2O (0.149 g), urea (0.180 g), and ammonium fluoride (0.037 g) was gently stirred for 15 min to dissolve all the precursor materials. The resultant solution was poured into a Teflon-lined steel autoclave containing a cleaned NF piece. After sealing the autoclave properly, the hydrothermal reaction was carried out at 120 °C for 6 h. Subsequently, the autoclave temperature was allowed to decrease naturally to room temperature (25–30 °C), and the resulting Zn-Co hydroxide precursor NW arrays (Zn-Co LDH NWs)-coated NF was picked out, cleaned, and subsequently dried for 24 h at 60 °C. After calcination at 350 °C for 2 h, the precursor NWs were transformed into ZnCo2O4 NWs. The MnCo2O4 NWs were also fabricated by a similar method, replacing the Zn salt with the Mn salt. The average deposited masses of ZnCo2O4 and MnCo2O4 NWs onto the NF were measured to be 2.2 and 1.4 mg cm−2, respectively.

2.2. Synthesis of hierarchical MCo2O4@Ni(OH)2 (M = Zn or Mn) core@shell nanohybrid arrays

The Ni(OH)2 nanosheets were grown onto the ZnCo2O4 core material using different hydrothermal reaction time (0.5, 1, and 2 h) for shell synthesis to obtain an optimal shell thickness. In a typical optimized synthesis procedure of ZnCo2O4@Ni(OH)2, a measured amount of NiCl2·6H2O and urea was added to distilled water and then stirred for 15 min to make a uniform solution. Then, the mixed solution was transferred into a Teflon-lined autoclave and a piece of ZnCo2O4 NW array (M = Zn or Mn)-coated NF was dipped into the solution. The autoclave was properly sealed and kept at 100 °C for 1 h. After cooling the autoclave, the resultant NF supported ZnCo2O4@Ni(OH)2 sample was cleaned and maintained in an oven at 65 °C for 24 h. For comparison, the MnCo2O4@Ni(OH)2 sample was also synthesized using a similar method as mentioned above. The mass loadings of ZnCo2O4@Ni(OH)2 and MnCo2O4@Ni(OH)2 nanoarrays were found to be 3.1 and 2.3 mg/cm2, respectively.

2.3. Synthesis of ZIF-derived porous nitrogen-doped carbon (PNC)

The 3D ZIF-8-derived porous nitrogen-based carbon was synthesized and used as a negative electrode. First, Zn(CH3COO)2·2H2O (4 mmol) and 2-methylimidazole (24.0 mmol) were separately dissolved by magnetic stirring in 35 mL and 15 mL methanol, respectively. Both solutions were separately kept on an ice-cold water chamber for 1 h. Next, the imidazole solution was added dropwise to the uniform solution of zinc acetate and then stirred at 25 °C for 10 min. Subsequently, the mixed solution was aged for 24 h at 25 °C. The as-obtained white ZIF-8 precipitate was then suspended in absolute ethanol, collected by centrifugation, and finally freeze-dried for 2 d. The PNC material was obtained as a black powder by annealing the ZIF-8 particles for 3 h at 800 °C under nitrogen atmosphere.

2.4. Material characterizations

The crystallinity of the manufactured samples was determined by X-
3. Results and discussion

The synthesis route for the fabrication of the core@shell material is schematically shown in Fig. 1. The 3D hierarchical NW arrays of the M-Co layered double hydroxide (M-Co LDH; M = Zn or Mn) precursors were grown onto the NF using a hydrothermal reaction in the presence of the metal precursor salt, urea, and ammonium fluoride. Next, the M-Co LDH NW arrays were annealed at 350 °C via a complex air oxidation procedure to construct the MCo2O4 NWs-coated NF. The as-obtained rough MCo2O4 NWs were then used as the skeleton support to grow ultra-thin Ni(OH)2 nanosheets during another hydrothermal reaction, driven by surface-energy reduction, to form MCo2O4@Ni(OH)2 nanohybrids.

The architectures and surface morphologies of the NF-supported MCo2O4 NWs and MCo2O4@Ni(OH)2 nanohybrids were investigated by field emission scanning electron microscopy (FESEM) analysis. Fig. 2a, d show the FESEM images of ZnCo2O4 and MnCo2O4, respectively. The entire NF surface is fully coated by the MCo2O4 NWs after hydrothermal reaction and successive calcination. The FESEM images reveal that the MCo2O4 NWs are highly aligned on the substrate, providing an ideal platform for the formation of Ni(OH)2 sheets. The oxide NWs show porous architecture, attributed to the elimination of H2O and CO2 during calcination. High- and low-magnification FESEM imagery of the ZnCo2O4@Ni(OH)2 nanohybrid arrays are shown in Fig. 2b and c, respectively, which reveal that the diameters of the ZnCo2O4@Ni(OH)2 heterostructures increase and the surfaces of the nanohybrids become wrinkled after assimilation of the Ni(OH)2 sheets onto the oxide NW arrays. In addition, the ZnCo2O4 NWs retain their inherent structural features after being orderly and uniformly decorated by the Ni(OH)2 sheets in the final core@shell structures. Notably, no Ni(OH)2 nanosheets are observed between the NWs, and the interconnected ultra-thin Ni(OH)2 nanosheets uniformly cover the outer surface of the ZnCo2O4 NWs in a twisting and crumpling manner. This produce a unique 3D hierarchical highly porous core@shell architecture. The distances between the adjacent interconnected nanosheets generate voids, resulting in an interconnected architecture that is ideal for fast electron transportation and ion diffusion [2,12]. Such a distinctive hierarchical architecture with open and free interspaces between the nanosheets enhances the area of contact between the electrolyte and electrode material and enables easy access of the electrolytes to the core materials. Furthermore, the combination of a Ni(OH)2 shell layer onto the 3D hierarchical ZnCo2O4 NW protects the core material during long-run charging-discharging cycles [19]. In contrast, in MnCo2O4@Ni(OH)2, the neighboring Ni(OH)2 sheets are in contact with each other, owing to the limited space between them. The thick/dense Ni(OH)2 nanosheet layer on the surfaces of the MnCo2O4 NWs can entirely mask the core material (Fig. 2e, f). Furthermore, Ni(OH)2 sheets were deposited within the gaps of the MnCo2O4 NWs, resulting in the agglomerated morphology of the MnCo2O4@Ni(OH)2 nanohybrid.

All the materials presented three strong XRD peaks at 44.68, 52.09, and 76.61°, ascribed to the typical XRD peaks of the NF (Fig. 3) [3]. The XRD peaks of the as-prepared ZnCo2O4 NWs are well-identified with JCPDS card 00-001-1149 of cubic ZnCo2O4 (Fig. 3a). The XRD patterns of the as-fabricated MnCo2O4 NWs (Fig. 3b) are similar to those of the planes of cubic MnCo2O4 as reported in JCPDS card 00–001–1130. The characteristic XRD pattern of Ni(OH)2, as reported in JCPDS card 00–001–0771, shows the most prominent peaks at 19.58°, assigned to the (001) plane. Other peaks at 34.3° and 38.75°, corresponding to the (100) and (101) planes, respectively, are also observed. These major Ni(OH)2 and ZnCo2O4 diffraction peaks are noticed in the XRD patterns of ZnCo2O4@Ni(OH)2 (Fig. 3a). Similarly, the diffraction pattern of MnCo2O4@Ni(OH)2 shows the presence of Ni(OH)2 and MnCo2O4 (Fig. 3b). The peak positions related to the Ni(OH)2 present in the core@shell material are broad, owing to the very small crystalline sizes of Ni(OH)2 [24]. In comparison to the XRD diffraction peaks of ZnCo2O4@Ni(OH)2, the peaks of MnCo2O4 are less prominent in the

where the time of discharge is denoted as ‘t’.
MnCo$_2$O$_4$@Ni(OH)$_2$ XRD pattern. In this case, the excess growth of the Ni(OH)$_2$ shell overshadow the MnCo$_2$O$_4$ peaks, corroborating the FESEM image. Peak shifting of the MnCo$_2$O$_4$ and Ni(OH)$_2$ materials is observed in our as-synthesized core@shell materials, as compared to their corresponding JCPDS patterns. XRD peak position shifting is generally found in multicomponent hybrid materials, and slightly shifted peak positions of Ni(OH)$_2$ over their related JCPDS patterns have been previously reported [17,24–26].

Because the SA, pore-diameter, and pore size distribution are important factors for electro-active nanostructured materials, Brunauer–Emmett–Teller (BET) nitrogen adsorption–desorption analyses were performed to evaluate these properties. The $N_2$ adsorption and desorption isotherms of all the samples were plotted and are shown in Fig. 3c and S1a. A characteristic IV-type isotherm with a distinct hysteresis loop is observed for all samples within the relative pressure ranging from 0.45 to 1.0 $P/P_0$, indicating their mesoporous character [22]. The BET specific SA values of ZnCo$_2$O$_4$, ZnCo$_2$O$_4$@Ni(OH)$_2$, MnCo$_2$O$_4$, and MnCo$_2$O$_4$@Ni(OH)$_2$ are determined as 62.0, 91.0, 60.7, and 70 $\text{m}^2\text{g}^{-1}$, respectively. An increment in the specific SA of the core@shell material is attributed to the presence of interconnected Ni(OH)$_2$ nanosheets on the core surface [2]. The high BET specific SA is advantageous for delivering more electro-active area for redox reaction. The pore-size distribution analyses of all the samples were performed using the Barrett-Joyner-Halenda (BJH) method, and the corresponding distribution analysis outcomes are displayed in Fig. 3d and S1b. These data show that the average pore size distributions for ZnCo$_2$O$_4$, ZnCo$_2$O$_4$@Ni(OH)$_2$, MnCo$_2$O$_4$, and MnCo$_2$O$_4$@Ni(OH)$_2$ are mainly centered at 3.87, 3.66, 3.92, and 3.95 nm, respectively, indicating the excellent mesoporosity of all these materials. The total pore volumes of ZnCo$_2$O$_4$, ZnCo$_2$O$_4$@Ni(OH)$_2$, MnCo$_2$O$_4$, and MnCo$_2$O$_4$@Ni(OH)$_2$ are determined as 0.14, 0.38, 0.13, and 0.20 $\text{cm}^3\text{g}^{-1}$, respectively. Specifically, ZnCo$_2$O$_4$@Ni(OH)$_2$ possesses the higher SA than the reported analogous core@shell material [2,17,19,20]. The high SA and pore volume expose more of the electro-active site for mass transport and redox reaction, thereby improving the charge-storage capacity of ZnCo$_2$O$_4$@Ni(OH)$_2$.

The detailed morphology of the ZnCo$_2$O$_4$ and ZnCo$_2$O$_4$@Ni(OH)$_2$ structures were further studied by transmission electron microscopy (TEM). The TEM image of a single ZnCo$_2$O$_4$ NW exhibits the porosity ascribed to the annealing of its mother element Zn-Co LDH (Fig. 4a). Notably, the TEM image (Fig. 4b) of ZnCo$_2$O$_4$@Ni(OH)$_2$ shows that the ultra-thin Ni(OH)$_2$ sheets are anchored onto the ZnCo$_2$O$_4$-embedded NF,
forming a unique core@shell architecture. The porous Ni(OH)₂ nanosheets with an average thickness of ~200 nm are uniformly grown over the ZnCo₂O₄ NW. This architecture reinforces Ni(OH)₂ nanosheet surfaces, providing more electro-active sites for electrochemical reaction. The fabrication of such unique ZnCo₂O₄@Ni(OH)₂ nanohybrid improves the conductivity and electron transport, thus boosting the rate performance and cyclic stability. The ZnCo₂O₄@Ni(OH)₂ shows fringe spacings of ~0.243 and 0.284 nm assigned to the (311) and (220) planes of ZnCo₂O₄ and Ni(OH)₂, respectively.

Fig. 3. (a) XRD patterns of (a) ZnCo₂O₄ and ZnCo₂O₄@Ni(OH)₂, and (b) MnCo₂O₄ and MnCo₂O₄@Ni(OH)₂. Plots of (c) N₂ sorption isotherms and (d) pore size distributions (BJH plots) of ZnCo₂O₄@Ni(OH)₂ and MnCo₂O₄@Ni(OH)₂.

Fig. 4. (a) TEM image of ZnCo₂O₄ nanowire. (b) TEM images of the ZnCo₂O₄@Ni(OH)₂ nanohybrid. (c) HRTEM images of the ZnCo₂O₄ core area. (d) HRTEM image of the Ni(OH)₂ shell area. (e) SAED pattern of the ZnCo₂O₄@Ni(OH)₂ nanohybrid. EDX color mapping for (f) Co, (g) Zn, (h) Ni, and (i) O.
ZnCo$_2$O$_4$, respectively, (Fig. 4c). The lattice spacings of ~0.454 and 0.227 nm are ascribed to the (001) and (101) crystal planes of Ni(OH)$_2$, respectively, (Fig. 4d). The SAED pattern of the core@shell material reveals bright spots and a typical ring pattern, demonstrating its crystalline character, and the diffraction rings are ascribed to the (311), (220), and (511) planes of ZnCo$_2$O$_4$ and (001) and (101) planes of Ni(OH)$_2$, as shown in Fig. 4e. Furthermore, EDX elemental mapping (Fig. 4f-i) confirms that the elements Zn and Co are concentrated in the core region, whereas O and Ni are dispersed in the whole area, thereby indicating ZnCo$_2$O$_4$@Ni(OH)$_2$ core@shell heterostructure formation.

X-ray photoelectron spectroscopy (XPS) was performed to attain further insight into the elemental oxidation states and compositions of ZnCo$_2$O$_4$@Ni(OH)$_2$ and MnCo$_2$O$_4$@Ni(OH)$_2$ materials. The survey spectra (Figs. S2a, b) of ZnCo$_2$O$_4$@Ni(OH)$_2$ and MnCo$_2$O$_4$@Ni(OH)$_2$ show the presence of the elements Co, Zn, Ni, and O and Co, Mn, Ni, and O, respectively. The Co 2p XPS spectrum (Fig. 5a) of ZnCo$_2$O$_4$@Ni(OH)$_2$ exhibits two prominent peaks at ~795.3 and 780.0 eV, corresponding to the Co 2p$_{3/2}$ and Co 2p$_{1/2}$, respectively, and two shake-up satellite peaks at ~796.3 (Co 2p$_{3/2}$) and 780.6 (Co 2p$_{1/2}$) eV, and two shake-up satellite peaks. Therefore, the Co 2p XPS spectra analyses confirm the presence of Co$^{2+}$ and Co$^{3+}$ states in ZnCo$_2$O$_4$@Ni(OH)$_2$ and MnCo$_2$O$_4$@Ni(OH)$_2$ materials. The XPS Zn 2p spectrum of ZnCo$_2$O$_4$@Ni(OH)$_2$ can be divided into two prominent peaks assigned to the Zn 2p$_{3/2}$ (1022.6 eV) and Zn 2p$_{1/2}$ (1045.7 eV) states, as shown in Fig. 5b [12]. It can be observed from the Fig. 5c that the Mn 2p spectrum is split into two peaks which are identified as Mn 2p$_{3/2}$ and Mn 2p$_{1/2}$ levels. The XPS Mn 2p spectrum pattern is nicely correlated with reported literature [29–32]. The broad Mn 2p$_{3/2}$ peak pattern suggests the probable charging effects and multiplet splitting have resulted in the line broadening [33]. The Ni 2p deconvoluted spectra of ZnCo$_2$O$_4$@Ni(OH)$_2$ and MnCo$_2$O$_4$@Ni(OH)$_2$ display two peaks at binding energies of ~855.6 and 873.5 eV, assigned to the Ni 2p$_{3/2}$ and Ni 2p$_{1/2}$ states (Fig. 5d), respectively [3,5]. Another two peaks at 861.7 and 879.5 eV are assigned as the shake-up satellite peaks of the Ni$^{2+}$ ion. Fig. 5e show the deconvoluted O1s spectra of ZnCo$_2$O$_4$@Ni(OH)$_2$ and MnCo$_2$O$_4$@Ni(OH)$_2$, respectively, where the two peaks at ~530.4 and 532.6 eV are attributed to the O$^{2-}$ ion in metal oxide phase and hydroxyl group, respectively, [17,19,31,34].

The electrochemical performances of all the binder-free NF-supported samples were investigated in a three-electrode measuring assembly using a 2 M aqueous KOH solution. The ZnCo$_2$O$_4$ NWs were used as a perfect scaffold to fabricate the complex core@shell architecture of ZnCo$_2$O$_4$@Ni(OH)$_2$. To obtain an optimal Ni(OH)$_2$ shell thickness on the ZnCo$_2$O$_4$ core, the shell was synthesized with varying hydrothermal reaction times (0.5, 1, and 2 h). Then, the tuning effect of the shell-formation reaction time on the electrochemical performance of the core@shell material was monitored by cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) analyses (Fig. S3). Accordingly, the electrochemical performances of these samples were co-related with their FESEM images to understand the role of shell thickness in manipulating the supercapacitive performance. Comparison of the electrochemical performances clearly indicates that a 0.5 h shell growth reaction time is insufficient to develop a uniform Ni(OH)$_2$ shell layer onto the ZnCo$_2$O$_4$ NW arrays (Figs. S4a-c). Accordingly, the core@shell material formed for the 0.5 h of shell-formation reaction time shows minimum capacity. A reaction time of 1 h is deemed optimal for the development of uniform Ni(OH)$_2$ shell layer over the core material. The well-covered Ni(OH)$_2$ shell layer allows easy infiltration of the electrolyte ions in the ZnCo$_2$O$_4$ NW arrays to deliver the maximum electrochemical outcome of the core@shell heterostructure (Fig. 2b-c). However, with the further increase in the hydrothermal reaction time to 2 h, the afforded ZnCo$_2$O$_4$@Ni(OH)$_2$ exhibits decreased supercapacitive performance due to the increase in shell thickness (Figs. S4d-f). As the Ni(OH)$_2$ shell thickness/density increases with increasing reaction time, the contribution of the core material to the overall capacity decreases. This is attributed to the higher shell thickness, which inhibits the uniform access of the electrolyte to the ZnCo$_2$O$_4$ NW arrays and decreases the overall electrochemical outcome of the ZnCo$_2$O$_4$@Ni(OH)$_2$ material. Hence, a hydrothermal reaction time of 1 h was selected as the optimum...
time to obtain perfect growth of the Ni(OH)2 shell layer onto the ZnCo2O4 core, and MnCo2O4@Ni(OH)2 was fabricated by following a similar synthesis protocol for comparison.

The CV plots of ZnCo2O4@Ni(OH)2, MnCo2O4@Ni(OH)2, ZnCo2O4, and MnCo2O4 at 10 mV s\(^{-1}\), across a potential range of 0.2–0.75 V were next investigated and compared (Fig. 6a). In each cathodic and anodic scan, all the electrode samples show distinct redox peaks, revealing their battery-type character and that the capacity is mainly governed by a redox mechanism \([8,19]\). The oxidation/reduction peaks at \(\approx 0.48/0.13, 0.43/0.15, 0.34/0.18, \) and \(0.31/0.21\) V (vs Ag/AgCl), observed at a scanning rate of 10 mV s\(^{-1}\), are assigned to the electrochemical Faradaic reactions of the ZnCo2O4@Ni(OH)2, MnCo2O4@Ni(OH)2, ZnCo2O4, and MnCo2O4 electrodes, respectively. The representative oxidation/reduction peaks of ZnCo2O4 and MnCo2O4 are primarily ascribed to the reversible electron transfer processes between the different valence states of the Co ion (Co\(^{2+}/\)Co\(^{3+}\)). However, for the core@shell material, the analogous oxidation and reduction peaks are due to the Faraday reversible redox reactions of Co\(^{2+}/\)Co\(^{3+}\) (core material) and Ni\(^{2+}/\)Ni\(^{3+}\) (shell material) in the presence of aqueous KOH solution \([2]\). As a result, compared to the ZnCo2O4 and MnCo2O4, the assimilation of the Ni(OH)2 shell onto the MCo2O4 NWs results in a higher current density and larger integrated CV curve area. Fig. 6b shows the CV outputs of ZnCo2O4@Ni(OH)2 at separate sweep rates (5–50 mV s\(^{-1}\)) within a fixed potential width range of –0.2 to 0.75 V. The typical reduction/oxidation peaks slightly shifted toward more positive and negative potential directions, respectively, upon raising the scan rate, which is attributed to the active material polarization \([22,35]\).

This also shows that the electro-active material exhibits a quick scan rate, which is attributed to the active material polarization \([22,35]\). The negative and positive potential directions, respectively, upon raising the scan rate, all the electrode samples show distinct redox peaks, revealing their battery-type character and that the capacity is mainly governed by a redox mechanism \([22,35]\). The oxidation/reduction peaks located at \(\approx 0.48/0.13, 0.43/0.15, 0.34/0.18, \) and \(0.31/0.21\) V (vs Ag/AgCl), observed at a scanning rate of 10 mV s\(^{-1}\), are assigned to the electrochemical Faradaic reactions of the ZnCo2O4@Ni(OH)2, MnCo2O4@Ni(OH)2, ZnCo2O4, and MnCo2O4 electrodes, respectively. The representative oxidation/reduction peaks of ZnCo2O4 and MnCo2O4 are primarily ascribed to the reversible electron transfer processes between the different valence states of the Co ion (Co\(^{2+}/\)Co\(^{3+}\)). However, for the core@shell material, the analogous oxidation and reduction peaks are due to the Faraday reversible redox reactions of Co\(^{2+}/\)Co\(^{3+}\) (core material) and Ni\(^{2+}/\)Ni\(^{3+}\) (shell material) in the presence of aqueous KOH solution \([2]\). As a result, compared to the ZnCo2O4 and MnCo2O4, the assimilation of the Ni(OH)2 shell onto the MCo2O4 NWs results in better electronic conductivity and electrochemical outputs. Furthermore, ZnCo2O4@Ni(OH)2 exhibits the highest effective SA with a smaller pore size, thereby providing a more electrochemically active SA for facile electron and ion transport at the electrolyte/electrode junction. More importantly, the presence of Zn element improves the electrical conductivity, mechanical flexibility, and chemical stability of the bimetallic oxide, thereby providing good mechanical support and electron transport channels to enhance the electrochemical storage capability of the ZnCo2O4@Ni(OH)2 heterostructures \([36]\).

Fig. S5 illustrates that the plots of the peak current density \(I_p\) anodic/cathodic values versus square root of the scan rates \((\nu^{1/2})\) at different scan rates for the ZnCo2O4@Ni(OH)2 and MnCo2O4@Ni(OH)2 electrodes. These plots show a linear relationship between \(I_p\) and \(\nu^{1/2}\) and properly match with the typical power-law relationship \((I_p = a\nu^b,\) where \(b = 0.5)\), suggesting a fully diffusion-controlled Faradaic reaction process for both the electrodes \([37–40]\).

GCD measurements of all the samples at different current densities (3–50 mA cm\(^{-2}\)), over the fixed potential window range of 0–0.45 V, were performed to compare their electrical charge-storage performances. The typical GCD plots of the ZnCo2O4@Ni(OH)2 core@shell material and other electrode materials are shown in Figs. 6c and S6, respectively. A consistent but divergent potential plateau area can be observed during the charging and discharging processes of all these samples, confirming their battery-type character, thereby corroborating with the CV results \([41]\). Furthermore, all the studied electrode materials display approximately symmetrical GCD curves at varied current densities, indicating the excellent reversibility of the Faraday reaction process and good capacitive characteristics \([11]\). The discharge time for the four electrodes follow the order: MnCo2O4 < ZnCo2O4 < MnCo2O4@Ni(OH)2 < ZnCo2O4@Ni(OH)2. To verify the superiority of the ZnCo2O4@Ni(OH)2 sample over the MnCo2O4@Ni(OH)2, ZnCo2O4, and MnCo2O4 samples, we determined the specific and areal capacities from the discharge part of the GCD plot. The areal/specific capacity values of all these samples at various areal current densities are depicted in Fig. 6d. The higher capacity value of the core@shell materials are ascribed to the increased electrochemical active SA and additional capacity supplied by Ni(OH)2. The synergistic effect within the hetero-nanostructure enhanced the charge-transfer process, thus improving the energy storage efficacy of the electro-active material \([18]\).

Notably, the areal and specific capacity values of the ZnCo2O4@Ni(OH)2 electrode are much higher than the other electrodes at different current densities.

Fig. 6. (a) CV curves of ZnCo2O4, MnCo2O4, MnCo2O4@Ni(OH)2, and ZnCo2O4@Ni(OH)2 at 10 mV s\(^{-1}\). (b) CV curves of the ZnCo2O4@Ni(OH)2 electrode at different scan rates. (c) Galvanostatic charge-discharge (GCD) plots of the ZnCo2O4@Ni(OH)2 electrode at different current densities. (d) Plot of specific/areal capacity vs current density for all the electrodes. (e) EIS Nyquist plots for all the electrodes at open circuit voltage (inset: equivalent circuit used to fit the data). (f) Cyclic performance and Coulombic efficiency of ZnCo2O4@Ni(OH)2 at a current of 40 mA cm\(^{-2}\) (inset: final 15 GCD cycles).
The ZnCo₂O₄@Ni(OH)₂ core@shell electrode shows superior areal capacity values as high as ~1.34, 1.25, 1.20, 1.14, 1.09, 1.01, 0.94, 0.82, 0.72, and 0.69 mAh cm⁻² under current densities of 3, 4, 6, 8, 10, 15, 20, 30, 40, and 50 mA cm⁻², respectively. The corresponding specific capacity values of this sample are ~ 432.6, 404.0, 386.0, 367.5, 352.0, 326.2, 303.8, 264.3, 231.3, and 224.0 mA h g⁻¹. All these electrodes show a decreasing trend in the capacity values with increasing areal current densities, owing to their internal resistances. Moreover, at higher current, the outer surface pores are mainly utilized, while most of the deeper electro-active pores are inaccessible during fast electrochemical reaction [22]. The capacity retention values of ZnCo₂O₄@Ni(OH)₂, MnCo₂O₄@Ni(OH)₂, ZnCo₂O₄, and MnCo₂O₄ are determined to be 52, 44.3, 45, and 33.4%, respectively, up to 50 mA cm⁻², indicating the higher rate capability of ZnCo₂O₄@Ni(OH)₂. Indeed, the well-covered ultra-thin Ni(OH)₂ nanosheets decrease the path lengths for electrolyte diffusion, increasing electrolyte ion migration during the fast charging-discharging reaction, thereby resulting in the higher rate capability of ZnCo₂O₄@Ni(OH)₂. Microstructural analysis reveals the development of excess Ni(OH)₂ sheets in MnCo₂O₄@Ni(OH)₂ compared to ZnCo₂O₄@Ni(OH)₂. The excess Ni(OH)₂ nanosheets in MnCo₂O₄@Ni(OH)₂ comprises a large effective SA; however, the highly dense Ni(OH)₂ sheets decrease the electrical conductivity of the hybrid material and prevent the electrolyte access into the core material, resulting in its lower electrochemical performance compared to that of ZnCo₂O₄@Ni(OH)₂ [19].

To investigate the innate electrochemical behavior (ionic/electrical conductivity) of the as-fabricated electrode material, electrochemical impedance spectroscopy (EIS) analysis was next executed, and the as-obtained Nyquist plots of the four electrodes are shown in Fig. 6e. All four EIS Nyquist spectra comprise a pseudo-semicircle part (high-frequency area) and an approximately straight diagonal line (low-frequency area). The internal resistance (R_i) charge-transfer resistance (R_q) values of ZnCo₂O₄, ZnCo₂O₄@Ni(OH)₂, MnCo₂O₄, and MnCo₂O₄@Ni(OH)₂ are determined to be 0.74/1.72, 0.61/0.60, 0.82/1.06, and 0.72/0.82 Ω, respectively. These resistance values together with the CV and GCD results confirm the superior electron transport, faster charge-transfer kinetics, and rapid ion penetration at the electrolyte/electrode junction of the core@shell electrode materials [42]. However, compared to the MnCo₂O₄@Ni(OH)₂ nanohybrids, the ZnCo₂O₄@Ni(OH)₂ nanohybrids exhibited lower solution resistance and quicker charge-transfer kinetics, owing to its structural advantage. At low frequency, ZnCo₂O₄@Ni(OH)₂ presented a straight line that is more vertical (higher slope) than those of the other electrode materials. This indicates better electrolyte infiltration (lower ion-diffusion resistance) into the ZnCo₂O₄@Ni(OH)₂ electrode, resulting in a greater number of rapid redox reactions and higher capacity [5,43].

Another important aspect is the cyclic stability performance measurement of the electrode material to check its durability and quality for practical application. We selected ZnCo₂O₄@Ni(OH)₂ core@shell electrode for cyclic stability test since it exhibits excellent electrochemical activity. To explore the cyclic performance of the ZnCo₂O₄@Ni(OH)₂ electrode, the specific capacity was estimated after long-run repeated GCD processes at 40 mA cm⁻² (Fig. 6f). After 5000 charging and discharging cycles, the retention rate of the initial capacity for ZnCo₂O₄@Ni(OH)₂ is 90%. The last 15 cycles of the 5000 GCD curves are depicted in the inset of Fig. 6f and indicate that the electrode material maintains its Faradic battery-type characteristics after 5000 cycles, indicating its excellent cycling stability. Furthermore, the linear areas under the charge/discharge GCD curve of 95–96% across the 5000 cycles, proving its excellent electrochemical activity. On the other hand, the ZnCo₂O₄ NWs-based electrode only retains 63.8% capacity after 5000 cycles, attributed to the absence of a protective coating (Fig. S7). The compositional and structural synergies between the ZnCo₂O₄ NWs and Ni(OH)₂ minimize the dissolution of the electrode material during long cyclic testing, resulting in good electrochemical stability. The free spaces (voids) between the neighboring Ni(OH)₂ nanosheets not only act as a perfect “ion reservoir chamber” to accelerate electrolyte diffusion but also prevent the breakdown of the hierarchical architecture, owing to the volume change caused by ion insertion/extraction during the charge-discharge process [8,17,44]. After the cyclic stability test, FESEM (Fig. S8a) analyses were performed to the ZnCo₂O₄@Ni(OH)₂ electrode material, in order to relate its morphological features to the durability. The FESEM image after cycling test show that the intrinsic morphology of the ZnCo₂O₄@Ni(OH)₂ electrode is well retained without any significant structural collapse, validating the good mechanical attachment with the current collector. However, the core@shell pattern becomes somewhat weakened after the stability test. Furthermore, the XRD peaks of Ni(OH)₂ becomes wider and weaker after the stability test of the core@shell material, as displayed in Fig. S8b. In comparison to the reported binary TMO@Ni(OH)ₓ [19] (Table S1), ZnCo₂O₄@Ni(OH)₂ shows superior electrochemical performance (specific capacity and cyclic stability), owing to the following factors: (i) The well-arrayed ZnCo₂O₄ NWs serve as a scaffold/support to enable the uniform development of the Ni(OH)₂ nanosheets, making the as-formed unique core@shell material completely electrochemically accessible. (ii) A higher amount of ZnCo₂O₄ breaks the layered structure of the shell material due to the formation of the undesirable spinel phase of the core material. In the present study, the optimized ZnCo₂O₄ NWs played a supportive role to prevent the breakdown of the core@shell assembly during the charging-discharging reaction, (iii) The optimized amount of ultra-thin Ni(OH)₂ nanosheets onto the ZnCo₂O₄ NWs enhance the unit-cell volume, increase the reversible capacity, and provide well-defined electron transportation pathways during electrochemical reaction. (iv) Maximum capacity contribution from the core material, owing to the easy infiltration of the electrolyte attained by the well-defined Ni(OH)₂ shell. (v) The mesoporous network of the as-synthesized hierarchical ZnCo₂O₄@Ni(OH)₂ material with a high SA and pore volume reduce the ion-diffusion/electron transport pathways and improve the charge storage capability [45].

The ZIF-derived highly porous 3D nitrogen-based carbon material was employed as a favorable negative electrode material to fabricate the solid-state ASC, owing to its excellent conductivity, ultra-high specific SA, and absolute porous morphology [46]. The as-synthesized PNC material was characterized using FESEM, TEM, and BET isotherms. The FESEM images show that the ZIF-8 sample comprises uniformly distributed rhombic dodecahedral crystals (Fig. 7a) [47,48]. The FESEM images (Figs. 7b, c) of PNC clearly reveal that the original shape (rhombic dodecahedral) of the ZIF-8 nanocrystals is well retained, even after carbonization. The TEM images (Fig. 7d) show the perfect rhombic dodecahedral-based morphology of the PNC material, which is coherent with the FESEM data. The PNC material shows a 3D hierarchical structure with an exclusive porous network and a high specific SA (1600 m² g⁻¹) (Fig. 7e), which improve the ion transport characteristics during electrochemical study [49].

As a negative electrode in the three-electrode assembly, the PNC electrode shows an excellent electric double-layer-type feature with a quasi-rectangular CV curve under a fixed voltage range (−1.0 to 0 V: Fig. 7f). With the rise in sweep-rate (from 10 to 100 mV s⁻¹), insignificant changes are observed in the shapes/patterns of the CV curves. In addition, the characteristic GCD plots of the PNC electrode material at a variety of areal current densities (2–50 mA cm⁻²) under a working potential range of −1.0 to 0 V are presented in Fig. 7g. All these GCD plots show near-symmetrical charge-discharge patterns with an insignificant IR drop value, suggesting superb Coulombic efficiency and low internal resistance. Furthermore, the linear areas under the charge/discharge GCD curve indicate typical electrochemical double layer capacitor (EDLC)-type behavior. The plots of the specific capacity values at various current densities are shown in Fig. 7h. The PNC electrode displays specific capacities as high as 49.2, 44.8, 43.2, 42.1, 40.7, 38.4, 36.1, 32.4, 29.5, and 27.0 mAh g⁻¹ at 2, 4, 6, 8, 10, 15, 20, 30, 40 and 50 mA cm⁻², respectively, indicating a 55% rate performance at 50 mA cm⁻². The cyclic stability test of the PNC electrode was performed for 5000 GCD cycles at a current density of 40 mA cm⁻² (Fig. 7i). Approximately 92%
of the original capacity is preserved by the PNC electrode after 5000 repeated GCD cycles, representing its outstanding cyclability. Furthermore, the EIS plot attained before the start of cycle testing was compared with that attained after the end of the cycle test to understand the electrochemical properties of the material (Fig. S9). There is no noticeable change in $R_s$ value, while the $R_{ct}$ value increased by ~2.7 Ω after the end of the cycle test. These superior electrochemical results indicate the application potential of the PNC as a negative electrode material for solid-state ASC devices.

To further study the possibility for practical utilization of the 3D ZnCo$_2$O$_4$@Ni(OH)$_2$ hierarchical nanohybrids and 3D PNC materials, ASC device was manufactured from ZnCo$_2$O$_4$@Ni(OH)$_2$ as positive and 3D porous PNC as negative electrode material using a KOH/PVA gel electrolyte. The CV plots for a three-electrode measuring assembly at a fixed scanning speed of 10 mV s$^{-1}$ for the negative and positive materials are depicted in Fig. 8a. The negative PNC electrode displays near-rectangular features in the CV curve across a potential width range of −1.0 to 0.0 V, confirming EDLC-type behavior. On the other hand, the ZnCo$_2$O$_4$@Ni(OH)$_2$ nanohybrid sample shows prominent redox peaks within a voltage range of −0.2 to 0.75 V, indicating battery-type character. The digital photographic images of the ASC device (ZnCo$_2$O$_4$@Ni(OH)$_2$//PNC) constructed using a split test cell are depicted in Fig. S10. The optimum potential window of the ASC device of 1.6 V is selected for electrochemical analysis. The CV plots at separate scan rates ranging from 10 to 50 mV s$^{-1}$ for a fixed potential range of 1.6 V are presented in Fig. 8b. The integrated CV curve area increases with the gradual increase in the scan rate; however, no noticeable changes are observed in the shapes of the typical CV curves. This indicates the high rate of electron transport and suitable capacitive character of the device [22]. The characteristic GCD plots of the ASC device over a fixed voltage range of 0–1.6 V at varied areal current density are shown in Fig. 8c. The symmetrical features of the GCD curves suggest the excellent Coulombic efficiency and good capacitive character of the ASC device. The specific capacity vs current density plot of the device is shown in Fig. 8d. The specific capacity values of the ZnCo$_2$O$_4$@Ni(OH)$_2$//PNC device are measured to be 97.8, 95.3, 94.7, 92.0, 88.7, 82.4, 76.3, 66.5, 58.0, and 50.5 mA h g$^{-1}$ at 4, 5, 6, 8, 10, 15, 20, 30, 40, and 50 mA cm$^{-2}$, respectively. Notably, ~52% of the capacity is retained by the device at a high current density of 50 mA cm$^{-2}$, indicating a good rate capability. Long-term cyclic stability testing (10,000 GCD cycles) of the device was further carried out at 40 mA cm$^{-2}$. Notably, the device shows a capacity decay of ~14% after 10,000 continuous GCD cycles (Fig. 8e), indicating outstanding cyclic stability. The inset in Fig. 8e depicts the first and last 15 GCD cycles of the total 10,000 cycles. Furthermore, the ZnCo$_2$O$_4$@Ni (OH)$_2$//PNC device shows excellent Coulombic efficiency (98–99.9%) throughout the cycling test.

The electrical energy storage capability of the ASC solid-state device was elucidated by estimating the energy and power densities. Fig. 8f shows the plot of energy density vs power density, which was identified as a typical Ragone plot. The ASC solid-state device manifests an ultra-
high gravimetric energy density of \( \sim 78.2 \text{ W h kg}^{-1} \) (maximum value) when the power density is 451 W kg\(^{-1}\). Furthermore, the device still delivers \( \sim 40.4 \text{ W h kg}^{-1} \) energy density at 4691 W kg\(^{-1}\) (maximum value) of power density. The above energy and power density values suggest excellent electrochemical performance of the solid-state ZnCo\(_2\)O\(_4\)@Ni(OH)\(_2\)//PNC device. The electrochemical performance of the solid-state ASC device was compared with the recently reported ASC devices, such as CuCo\(_2\)O\(_4\)@Ni(OH)\(_2\)//CFC//AC/CFC [18], CoMoO\(_4\)@Ni(OH)\(_2\)//OMEP//AC [20], Co\(_2\)O\(_3\)@Ni(OH)\(_2\)//AC [21], CuCo\(_2\)O\(_4\)@Ni(OH)\(_2\)//AC [42], CoS\(_2\)@Ni(OH)\(_2\)//AC [43], H-TiO\(_2\)@Ni(OH)\(_2\)//N–C [44], ZnCo\(_2\)O\(_4\)@Ni(OH)\(_2\)//AC [45], NiCo\(_2\)S\(_2\)@Ni(OH)\(_2\)//AC [50], NiC\(_6\)O@C@Ni(OH)\(_2\)//AC [51], ZnCo\(_2\)O\(_4\)@NiCo\(_2\)O\(_4\)//AC [52], NiCo-LDH/rGO//AC [53], NiCoO\(_2\)//NiCoP-20//AC [54], NiCo\(_2\)O\(_4\)//NiCo-LDH-G//AC [55], and VN/MoS\(_2\)//TiN/MnO\(_2\) [56]. The electrochemical outcome of the as-assembled device outperforms the above reported device systems (Table S2 and Fig. 8f) except NiCo\(_2\)O\(_4\)//NiCo-LDH-G//AC. However, the electrochemical performance of the NiCo\(_2\)O\(_4\)//NiCo-LDH-G//AC [55] device is comparable with our fabricated solid-state ASC device. This outstanding electrochemical storage performance of the ZnCo\(_2\)O\(_4\)@Ni(OH)\(_2\)//PNC device is attributed to the proper design and assembling of the electro-active materials. Furthermore, the outstanding cooperative interaction within the hierarchical 3D ZnCo\(_2\)O\(_4\)@Ni(OH)\(_2\) nanoarrays and highly porous 3D PNC material leads to rapid ion diffusion and electron transfer, resulting in improved electrochemical activity and structural integrity. These results reveal the huge potential of the as-created ASC solid-state device as a favorable advanced energy-storage device.

4. Conclusion

In summary, we have rationally designed and successfully fabricated well-aligned hierarchical MC\(_{x}\)O\(_{y}\)@Ni(OH)\(_{z}\) (\( M = \text{Zn or Mn} \)) multi-component core@shell structures on a conductive NF substrate, by changing the core composition using a simple three-step process. Among the as-synthesized MC\(_{x}\)O\(_{y}\)@Ni(OH)\(_{z}\) nanohybrids, the ZnCo\(_{x}\)O\(_{y}\)@Ni(OH)\(_{z}\) nanoarrays show unique nanopine forest-like morphology, high surface area (91 m\(^2\) g\(^{-1}\)) and pore volume. The ZnCo\(_{x}\)O\(_{y}\)@Ni(OH)\(_{z}\) electrode exhibits a superior supercapacitive performance, with a high specific capacity of 432.6 mAh g\(^{-1}\) at 3 mA cm\(^{-2}\), superior capacity retention of 90% after 5000 cycles, and lowest charge-transfer resistance. Furthermore, an ASC solid-state device was designed using ZnCo\(_{x}\)O\(_{y}\)@Ni(OH)\(_{z}\) positive electrode and PNC negative electrode. The device exhibits an energy density of 78.2 W h kg\(^{-1}\) at 451 W kg\(^{-1}\) power density and held a significant energy density of 40.4 W h kg\(^{-1}\) at a high power density of 4691 W kg\(^{-1}\). Our simple and practical synthetic strategy to tune the morphology, physicochemical properties, and electrochemical performance of electro-active materials may stimulate the fabrication of various core@shell architectures, hopefully creating more prospects for energy storage applications.

CRediT authorship contribution statement

Erdenebayar Baasanjav: Conceptualization, Investigation, Methodology, Writing – original draft. Parthasarathi Bandyopadhyay: Conceptualization, Methodology, Writing – original draft, Writing – review & editing, Supervision. Jung Sang Cho: Formal analysis, Data curation, Validation, Supervision. Sang Mun Jeong: Project administration, Writing – review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea Government (MSIT) (No. 2019R1A2C1086075; 2021R1A4A2001687). This work was also
supported from Chungbuk National University BK21 program (2021).

References


