Materials Research Express

PAPER

Multi-shelled Ni₆MnO₈ hollow microspheres for high-performance supercapacitors

Xiaoyu Liu, Jun Cao, Cheng Huang, Zhangxian Chen, Xiaoming Fan, Kun Shi, Zeheng Yang and Weixin Zhang

School of Chemistry and Chemical Engineering, Hefei University of Technology, Anhui Key Laboratory of Controllable Chemical Reaction & Material Chemical Engineering, Hefei, Anhui 230009, People’s Republic of China

Authors to whom any correspondence should be addressed.
E-mail: zehengyang@hfut.edu.cn and wxzhang@hfut.edu.cn

Keywords: Ni₆MnO₈, multi-shelled hollow microspheres, step by step adsorption, supercapacitor

Supplementary material for this article is available online

Abstract

Binary transition metal oxides have attracted tremendous interest for their excellent redox activity and large natural abundance. They could achieve distinct electrochemical properties by engineering special hollow structures. In this work, we have synthesized triple-shelled Ni₆MnO₈ hollow microspheres constructed with nanosheets through step by step adsorption of the corresponding metal ions on carbon spheres followed by calcination in air. The as-prepared Ni₆MnO₈ hollow microspheres with nanosheet shells have an average diameter of ~900 nm, with a large surface area of 145.011 m² g⁻¹. They exhibit outstanding capacitive performance as electrode materials, including high specific capacitance (1380 F g⁻¹ at 1 A g⁻¹), distinguished rate capability (68% capacity retention at ultrahigh 100 A g⁻¹) and stable cycling property (98% retention rate at 10 A g⁻¹ after 5000 cycles), which are superior to those of the Ni₆MnO₈ hollow microspheres with nanoparticle shells.

Furthermore, the assembled Ni₆MnO₈-NS/AC asymmetric supercapacitor demonstrates a high energy density (31.8 W h kg⁻¹ at 750 W kg⁻¹) with a high capacity retention of 93% even after 10,000 cycles. The distinguished performances can be attributed to the synergy of binary metals and the unique hollow structure with nanosheet shells.

1. Introduction

Due to the rapid depletion of traditional fossil energy and the intensifying pollution problems, the ever-increasing demand for sustainable and renewable energy has stimulated researchers to explore efficient and green energy storage materials [1]. Supercapacitors belong to new storage devices between secondary batteries and traditional capacitors [2] that have the superiorities of high power and energy density, low maintenance cost, long service life etc [3–6]. In recent years, transition metal oxides (TMOs) such as NiO [7] Mn₃O₄ [8] and WO₃ [9] have aroused great interest in recent years on account of their high redox activity and reduced activity energy of electron transfer process, and have been comprehensively investigated in energy storage field as pseudocapacitive electrode materials for supercapacitors [10–12].

Binary transition metal oxides (BTMOs) with more effective and quicker charge transfer in the materials show excellent electrochemical performance owing to the complex composition and the synergy of different elements compared with TMOs [13, 14]. The conductivity of metal oxides can be improved by doping other metals, thus BTMOs possess good electrical conductivity, which avail the charge transportation to current collector and improve the charge storage performance of supercapacitors [15]. However, there are some problems of structural instability, poor high-rate performance and unstable cyclic stability with BTMOs [1, 16]. One reason is that electrodes preparation through slurry-casting will inevitably bury some surfaces of active materials, especially those powder materials with micro- or nano-sized particles, therefore, restricting...
electrolyte access to surface-redox sites [17]. And another reason is that the particles of BTMOs pulverize readily due to volume change during charge-discharge process, which deteriorates the rate and cycling performance [1].

Hollow structured electrode materials for supercapacitors have shown considerable advantages. Their large specific surface area can augment the contact area between active material and electrolyte, thus affording more active sites for faradaic reactions [18–20]. Porous shells can increase the penetration of electrolyte and shorten the transmission distance of ions, leading to rapid reaction kinetics [2, 21]. Void space can adjust the pronounced volume change accompanied with repetitious charging/discharging processes, which is conducive to improve structural stability [22]. Therefore, designing appropriate structure and morphology of BTMOs to enhance their performances is particularly crucial.

Normally, BTMOs hollow structures can be generated by template-based method, based on soft template, self-template, or hard template [13, 23, 24]. Bubbles, micelles/vesicles, emulsions, etc can be used as soft template [25], which plays the part of structure-directing agent in the synthesis process [13]. For examples, Zhu et al prepared mesoporous NiCo2O4 hollow spheres with PVP as a facile soft-template [26]. Ensaït et al designed onion-like CuCo2O4 hollow microspheres with a diameter of about 1 μm by using bimetal-organic frameworks as a self-template [27]. The flexible multi-shelled soft templates such as vesicle are easily destroyed by changing parameters whereas the success for the conversion of single-shelled to multi-shelled hollow microspheres is limited for self-template method [28].

General synthesis of multi-shelled BTMOs hollow microspheres is still a great challenge [29]. Fortunately, hard template method has proven its versatility to the synthesis of multi-shelled hollow microspheres and control of the product morphology and structure, and the hard templates such as monodispersed polymers, silicon spheres [30, 31] and carbon spheres [32, 33] can be removed selectively by etching or thermal decomposition [22]. For example, multi-shelled (Co2/3Mn1/3)(Co5/6Mn1/6)2O4 hollow microspheres can be synthesized by doping Mn into Co3O4, leading to the change of crystalline rate of precursor with carbon spheres as hard-template [17]. By using citric acid as a chelating agent to inhibit hydrolysis and precipitation, multi-shelled Fe2(MoO4)3, NiMoO4 and MnWO4 hollow microspheres have been reported via coabsorption of negative and positive metal ions with citric acid as a chelating agent based on carbon spheres as hard-template [20].

In this work, we demonstrated the synthesis of multi-shelled Ni6MnO8 hollow microspheres constructed with nanosheets (denoted as Ni6MnO8-NS) for the first time through step by step adsorption of manganese and nickel ions on carbon microspheres. For comparison, multi-shelled Ni6MnO8 hollow microspheres constructed with nanoparticles (denoted as Ni6MnO8-NP) were also prepared through one-step adsorption of the corresponding metal ions on carbon microspheres. Both approaches are easy to control the morphologies of the final product without use of any agent. The Ni6MnO8-NS electrode material exhibits superior supercapacitor performance to the Ni6MnO8-NP counterpart for having larger specific surface area and more porosity due to its multi-shelled hollow microspheres with nanosheet shells. The successful synthesis of Ni6MnO8 samples increases the diversity of functional materials with multi-shelled hollow microspheres. Moreover, the proposed step-by-step adsorption strategy to construct multi-shelled hollow structure of binary transition metal oxides provides a new approach for the structural design of functional materials and has a good application prospect in energy conversion and storage.

2. Experimental section

2.1. Synthesis of multi-shelled Ni6MnO8 hollow microspheres

Sucrose (AR), hexahydrate nickel chloride (98%, AR), tetrahydrate manganese chloride (99%, AR) and urea (99%, AR) were all bought from Sinopharm Chemical Reagent Co., Ltd All reagents employed in the synthesis were used without further purification.

Synthesis of carbon spheres: Carbon spheres were synthesized through the polycondensation reaction of sucrose under hydrothermal condition [7]. The sucrose (13.86 g) was dissolved in deionized water (135 ml) by magnetic stirring until the solution becomes transparent. Subsequently, the above clear solution was put into a Teflon-lined stainless autoclave (150 ml) and then hydrothermally treated at 190 °C for 120 min. The obtained brown product was washed with deionized water three times and ethanol three times respectively, then naturally cooling down to environment temperature, and dried at 70 °C for 10 h in a vacuum oven.

Synthesis of multi-shelled Ni6MnO8 hollow microspheres assembled with nanosheets (Ni6MnO8-NS): Freshly-prepared carbon spheres (0.16 g) were added into a 10 ml MnCl2 aqueous solution (0.005 M) under sonication for 30 min and stirred for 30 min. Then 0.2 g urea was added into it as a precipitant and continued stirring for 30 min. After that, the mixed solution was left for 9 h in a water bath (90 °C) by magnetic stirring. Afterwards the resultant powder was collected by centrifugation, washed several times with deionized water and ethanol, followed by drying at 70 °C overnight. Subsequently, the above dark brown powder was dispersed into
60 ml of NiCl₂ aqueous solution (0.005 M) by sonication for 30 min and magnetic stirring for another 30 min. The remaining treatment procedures were the same as the first step, but with addition of 0.8 g urea. The Mn(OH)₂/C@Ni(OH)₂ composite precursor was formed after the step by step adsorption and precipitation. Finally, Ni₆MnO₈-NS sample was generated by heating the composite precursor to 600 °C with temperature ramping rates of 3 °C·min⁻¹ and then keeping at 600 °C for 3 h in air.

Synthesis of multi–shelled Ni₆MnO₈ hollow microspheres constructed with nanoparticles (Ni₆MnO₈-NP): Carbon spheres (0.16 g) were added in a mixture aqueous solution of NiCl₂ (0.005 M, 60 ml) and MnCl₂ aqueous solution (0.005 M, 10 ml) by sonication for 30 min and magnetic stirring for another 30 min, subsequently 0.8 g urea was added. The remaining treatment procedures were the same as the previous ones. After co-precipitation of Ni and Mn ions on carbon spheres, Ni(OH)₂-Mn(OH)₂/C composite precursor was yielded, which was further converted into Ni₆MnO₈-NP hollow microspheres through the identical calcination.

2.2. Materials characterization
The X’ Pert PRO MPD x-ray diffractometer using a Cu Kα radiation (λ = 0.15406 nm) at room temperature was employed to determine the crystallographic structure by acquiring x-ray diffraction (XRD) patterns. Field-emission scanning electron microscope (FESEM, Hitachi SU8020) was used to characterize the morphology. Microstructure was investigated using a transmission electron microscope (TEM) on a JEM-1400flash transmission electron microscope. A field emission transmission electron microscope (JEM-2100F) was used for characterization of high-resolution transmission electron microscopy (HRTEM), elemental mapping and selected area electron diffraction (SAED). The surface area of the multi-shelled Ni₆MnO₈ hollow spheres was analyzed with nitrogen adsorption measurements using the multi-point Brunauer–Emmett–Teller (BET) equation and the Barrett–Joyner–Halenda (BJH) method was used to calculate the pore size distribution of samples. X-ray photoelectron spectra (XPS) was obtained on a photoelectron spectrometer (ESCALAB250Xi) using Al Kα radiation.

2.3. Electrochemical measurements
The as-prepared Ni₆MnO₈ samples (active materials), conductive acetylene black, and polytetrafluoroethylene (PTFE) binder in 80%: 10%: 10% weight ratio with moderate ethanol as a solvent were mixed to fabricate the working electrodes. The slurry of the above mixture was pressed into the current collector (Ni foam), then dried in a vacuum oven overnight at 60 °C. In a three-electrode system, the reference electrode was Hg/HgO electrode, with platinum sheet as the counter electrode in the meantime, and using 6 M KOH aqueous solution as electrolyte. In order to test the capacitive properties of the material, it was electrochemically characterized on an electrochemical work station (CHI660E, Chennhua, Shanghai) by cyclic voltammetry (CV) test in potential range (0 to 0.6 V), galvanostatic charge-discharge (GCD) measurement in potential range (0 to 0.5 V) and an electrochemical impedance spectroscopy (EIS). According to the following equation, the charge-discharge curves are used for calculating the specific capacitance:

\[ C = \frac{I \Delta t}{m \Delta V} \]  \hspace{1cm} (1)

Among them, \( C \) (F g⁻¹), \( I \) (A), \( m \) (g), \( V \) (V), and \( t \) (s) represent the specific capacitance, the discharge current, the mass of single electrode active materials, potential difference of discharge, and discharge time, respectively.

The asymmetric supercapacitor (ASC) in a two–electrode system was assembled with the as-synthesized Ni₆MnO₈ materials as anode electrodes and active carbon materials (AC) as cathode electrode. All measurements of electrochemical property were also on the CHI660E device and the electrolyte was 6 M KOH aqueous solution. Using following equations, the energy density \( (E_d, \text{W h kg}^{-1}) \) of electrode material and the power density \( (P_d, \text{W kg}^{-1}) \) were calculated on basis of the mass of two asymmetric electrodes [34]:

\[ E_d = \frac{C(V \Delta V)^2}{2} \] \hspace{1cm} (2)

\[ P_d = \frac{E_d}{\Delta t} \] \hspace{1cm} (3)

3. Results and discussion
In order to determine the crystallographic structure of the two samples prepared via step by step adsorption approach and one-step adsorption approach, respectively, x-ray diffractometer was used for characterization analysis. Their XRD patterns (figure 1) could be indexed to cubic murdochite-type Ni₆MnO₈ (JCPDS 42-0479) in good agreement. The main diffraction peaks detected at 18.5°, 37.5°, 43.5°, 63.3° and 75.9° correspond to the reflection planes of (111), (222), (400), (440) and (622) of Ni₆MnO₈ (JCPDS 42-0479), respectively.
The morphology of Ni₆MnO₈ products and their corresponding precursors were observed by FESEM images (figure 2). The Mn(OH)₂/C@Ni(OH)₂ precursor (figure 2(a)) synthesized via step by step adsorption of the metal ions on carbon microspheres, is composed of large scale of 3D flower-like microspheres with an average diameter of about 1.4 μm, which are constructed of many uniform nanosheets with depth of about 200 nm. And the FESEM and TEM images of carbon microspheres are shown in figures S1(a) and (b) is available online at stacks.iop.org/MRX/7/065502/mmedia, respectively. Figure 2(b) reveals the morphology of the Ni(OH)₂-Mn(OH)₂/C composite precursor prepared via one step adsorption of the metal ions on carbon microspheres, which exists in microspheres of about 800–900 nm in diameter with relatively smooth surfaces. The morphological difference of the Mn(OH)₂/C@Ni(OH)₂ and the Ni(OH)₂-Mn(OH)₂/C precursors was attributed to their precipitation style. As for step by step adsorption approach, the Mn(OH)₂/C@Ni(OH)₂ precursor was synthesized with the manganese hydroxide yielded first on the carbon microspheres and then covered by the nickel hydroxide during the subsequent precipitation. Since Ni(OH)₂ usually grows in nanosheet habit, while Mn(OH)₂ prefers to grow into irregular plates [35, 36], the nickel hydroxide with nanosheet structure, which is formed during the second step, dominates the final morphology of the Mn(OH)₂/C@Ni(OH)₂ composite precursor. Figures S2(a) and (b) display the TEM images of Mn(OH)₂/C@Ni(OH)₂ precursor. However, for the Ni(OH)₂-Mn(OH)₂/C precursor synthesized through one step co-precipitation approach, the final morphology is governed by the two metal hydroxides. The sample does not exist in flower-like microspheres with nanosheet surface, but in microspheres with smooth surface, which

![Figure 1. XRD patterns of the two samples prepared via step by step adsorption approach and one-step adsorption approach, respectively: (a) Ni₆MnO₈-NS and (b) Ni₆MnO₈-NP.](image1.png)

![Figure 2. FESEM images of the precursors and products: (a) Mn(OH)₂/C@Ni(OH)₂ precursor, (b) Ni(OH)₂-Mn(OH)₂/C precursor, (c) Ni₆MnO₈-NS product, (d) Ni₆MnO₈-NP product.](image2.png)
are assembly with many merged nanoparticles (as shown in the inset of figure 2(b)). Figures S2(c) and (d) show the TEM images of Ni(OH)$_2$-Mn(OH)$_2$/C precursor, which exists in solid microspheres with smooth surfaces, significantly different from the Mn(OH)$_2$/C@Ni(OH)$_2$ precursor.

Both of the Mn(OH)$_2$/C@Ni(OH)$_2$ and Ni(OH)$_2$-Mn(OH)$_2$/C precursors were converted into Ni$_6$MnO$_8$ hollow microspheres with removal of the carbon template after calcination at 600 °C for 3 h in air. It can be seen that the Ni$_6$MnO$_8$-NS sample retains the flower-like microsphere morphology, still with nanosheet surfaces, and the Ni$_6$MnO$_8$-NP sample exists in microspheres with surface of many merged particles. The broken spheres inset in figures 2(c) and (d) reveal the hollow structure characteristics. The diameters of the hollow microspheres respectively shrink to about 900 nm and 500 nm for the Ni$_6$MnO$_8$-NS sample and the Ni$_6$MnO$_8$-NP sample due to high temperature calcining and removal of the carbon microsphere template.

The morphology and structure of the Ni$_6$MnO$_8$-NS hollow microspheres were further characterized by TEM and HRTEM observation. TEM images (figure 3(a)) show that the Ni$_6$MnO$_8$-NS sample, which was derived from the Mn(OH)$_2$/C@Ni(OH)$_2$ precursor prepared through step by step adsorption of the metal ions on carbon microspheres, displays triple-shelled microspheres morphology with nanosheet surfaces (shells). The formation of triple-shelled hollow microspheres can be explained as following. The carbon microspheres with adsorbed binary metal ions were burned gradually during the calcining process. Meanwhile, the amorphous binary metal oxides were transformed into crystalline phases and grew to form shells from outside to inside. The difference between the burning shrinkage rate of internal carbon microspheres and the crystallizing rate of external transition metal oxide layers leads to the formation of multi-shelled structure [17].

HRTEM image in figure 3(b) demonstrates the explicit lattice fringe with a d-spacing of 0.24 nm, in accordance with the (222) crystal facet of the cubic Ni$_6$MnO$_8$. In addition, the polycrystalline properties of the Ni$_6$MnO$_8$-NS sample were proved by electron diffraction pattern, as shown in figure 3(c). Furthermore, the series of concentric rings observed in the SAED pattern can be assigned to the (111), (222), (400), (440), (622), (444), (800), (840) and (931) planes of Ni$_6$MnO$_8$. To investigate the composition and distribution of binary metallic elements in the hollow microspheres, EDS spectrum and mapping were conducted. The EDS spectrum in figure 3(d) displays that the atomic percentages of Ni$_6$MnO$_8$ for Ni and Mn are 40.98% and 7.17%, respectively. And the atomic ratio of Ni and Mn is close to 6:1 of the target product Ni$_6$MnO$_8$. Elemental mapping in figure 3(e) indicates the multi-shelled hollow structure with homogeneous elemental distribution of Ni, Mn and O.

The same measurements were accomplished for the Ni$_6$MnO$_8$-NP sample by contrast. Figure 3(f) exhibits the TEM image of Ni$_6$MnO$_8$-NP sample, which was derived from the Ni(OH)$_2$/Mn(OH)$_2$/C precursor prepared through one step adsorption of the metal ions on carbon microspheres. Triple-shelled hollow microspheres were also observed, but the surfaces of the hollow microspheres were constructed of nanoparticles. Figure 3(g) shows an interplanar spacing of 0.20 nm, in keeping with the (400) lattice plane of the cubic Ni$_6$MnO$_8$. The concentric rings in the SAED pattern (figure 3(h)) can be assigned to the (111), (222), (400), (440), (622), (444), and (840) planes of polycrystalline Ni$_6$MnO$_8$. Figure 3(i) indicates that the atomic percentages of Ni and Mn are 39.55% and 6.82%, the atomic ratio of Ni$_6$MnO$_8$-NP for Ni and Mn is close to 6:1. The elemental distribution of Ni, Mn and O are uniform on the hollow microsphere, as shown in figure 3(i).

XPS was used for analyzing the elemental constitution and corresponding valence states of the hollow microsphere products. Figure 4 demonstrates the XPS spectra of the multi-shelled Ni$_6$MnO$_8$-NS hollow microspheres. The spectrum manifests the presence of Ni, Mn, and O elements in the product (figure 4(a)). For Ni 2p emission spectra (figure 4(b)), the peaks observed at 854.5 eV and 856.4 eV (belonging to Ni 2p$_{3/2}$) are allocated to Ni$^{2+}$, and the peak of Ni 2p$_{1/2}$ observed at 873 eV is also attributed to Ni$^{2+}$ [16, 37, 38]. Figure 4(c) shows that the binding energy at 654.3 eV (corresponding to Mn 2p$_{3/2}$ level) and 644.4 eV (belonging to Mn 2p$_{3/2}$ level) are attributed to Mn$^{2+}$, and that the peak of Mn$^{4+}$ is at 642.4 eV (Mn 2p$_{3/2}$ level) [11, 16, 38]. The O 1s spectrum located at 530 eV and 531.7 eV are associated with metal-oxygen bonds and −OH groups [38], respectively (figure 4(d)).

Figure 5 shows the surface area and corresponding porosity data of the different Ni$_6$MnO$_8$ hollow microsphere products. According to the IUPAC classification, the Nitrogen adsorption-desorption curves of Ni$_6$MnO$_8$-NS and Ni$_6$MnO$_8$-NP samples both belong to a type IV isotherm [39], which has hysteresis loops and exist in spherical materials mostly. The BJH pore-size distribution (insets) was tested for further research. It can be seen that the pore size is distributed mainly in 5–40 nm range and the curves exhibit typical mesoporous characteristics.

Table 1 lists the surface area, total pore volume and average pore size of the as-prepared Ni$_6$MnO$_8$ samples. The triple-shelled Ni$_6$MnO$_8$-NS samples have a high specific surface area (145.011 m$^2$ g$^{-1}$) owning to its triple-shelled hollow structure and the flower-like nanosheet surfaces, much higher than that of the Ni$_6$MnO$_8$-NP sample (70.129 m$^2$ g$^{-1}$). The Ni$_6$MnO$_8$-NS sample also shows a large total pore volume of 1.140 cm$^3$ g$^{-1}$ with an average pore size of 3.064 nm, while the Ni$_6$MnO$_8$-NP sample exhibits a smaller total pore volume of 0.336 cm$^3$ g$^{-1}$ with a bigger average pore size of 13.672 nm. From the inset (figure 5(a)), it can be seen that although the
Ni$_6$MnO$_8$-NS sample has a small average pore size, it still has some ratio of large pores ranging from 20 nm to 70 nm. The Ni$_6$MnO$_8$-NP sample has relatively narrower pore size distribution, mostly ranging from several nanometers to 40 nm. The triple-shelled Ni$_6$MnO$_8$-NS sample with higher specific surface area, bigger total pore volume, and more appropriate pore size distribution is beneficial to enhancing its supercapacitive performance when used as electrode materials.

Figure 3. Characterization of Ni$_6$MnO$_8$ samples: (a) TEM image of Ni$_6$MnO$_8$-NS, (b) HRTEM image of Ni$_6$MnO$_8$-NS, (c) corresponding SAED pattern of Ni$_6$MnO$_8$-NS, (d) EDS spectrum of Ni$_6$MnO$_8$-NS, (e) element mappings of Ni$_6$MnO$_8$-NS, (f) TEM image of Ni$_6$MnO$_8$-NP, (g) HRTEM image of Ni$_6$MnO$_8$-NP, (h) corresponding SAED pattern of Ni$_6$MnO$_8$-NP, (i) EDS spectrum of Ni$_6$MnO$_8$-NP, (j) element mappings of Ni$_6$MnO$_8$-NP.
The supercapacitive properties of the as-synthesized triple-shelled Ni$_{6}$MnO$_8$ hollow microspheres as electrode materials of supercapacitors were studied using CV, GCD and EIS measurements by a three-electrode electrochemical configuration. Figure 4 displays the CV curves of the triple-shelled Ni$_{6}$MnO$_8$-NS electrodes, which were tested at 5 mV s$^{-1}$ to 100 mV s$^{-1}$ sweep rate in the voltage window range from 0.0 V to 0.6 V (versus Figure 4.XPS spectra of multi-shelled Ni$_{6}$MnO$_8$-NS hollow microspheres: (a) Survey spectrum, (b) Ni 2p spectrum, (c) Mn 2p spectrum, and (d) O 1s spectrum.

Figure 5. Nitrogen adsorption-desorption curves and BJH pore-size distribution plots (insets) of samples: (a) Ni$_{6}$MnO$_8$-NS and (b) Ni$_{6}$MnO$_8$-NP.

Table 1. Surface area and porosity data for Ni$_{6}$MnO$_8$-NS and Ni$_{6}$MnO$_8$-NP samples.

| Sample         | Surface area (m$^2$ g$^{-1}$) | Total pore volume (cm$^3$ g$^{-1}$) | Average pore size (nm) |
|----------------|-------------------------------|-------------------------------------|------------------------|
| Ni$_{6}$MnO$_8$-NS | 145.011                       | 1.140                               | 3.064                  |
| Ni$_{6}$MnO$_8$-NP | 70.129                        | 0.336                               | 13.672                 |

The supercapacitive properties of the as-synthesized triple-shelled Ni$_{6}$MnO$_8$ hollow microspheres as electrode materials of supercapacitors were studied using CV, GCD and EIS measurements by a three-electrode electrochemical configuration. Figure 6(a) displays the CV curves of the triple-shelled Ni$_{6}$MnO$_8$-NS electrodes, which were tested at 5 mV s$^{-1}$ to 100 mV s$^{-1}$ sweep rate in the voltage window range from 0.0 V to 0.6 V (versus...
Hg/HgO). The curves exhibit obvious redox peaks, accounting for the representative pseudocapacitive behavior, which can be attributed to the redox reaction M-O or M-O-OH (M represent Ni or Mn) with the OH\(^-\) ions in KOH alkaline electrolyte \([40]\). The cathodic peak and anodic peak shift as scan rates increase because of the polarization influence on the electrode. According to the power law, the relation between the current and potential scan rate can be generally expressed as: 

\[ i(V) = \nu^b \]

where \( i \) means the current, \( \nu \) represents the scan rate, and both \( a \) and \( b \) are adjustable values. Based on the \( b \)-value of 0.5 and 1, two different electrochemical behaviors can be defined for electrochemical energy storage. With a \( b \)-value of 0.5, the current is controlled by semi-infinite linear diffusion, whereas with a \( b \)-value of 1, the current is surface-controlled, or capacitive behavior, indicating the redox pseudocapacitance contribution to overall charge storage \([9, 41]\). To evaluate the electrochemical behavior of the multi-shelled Ni\(_6\)MnO\(_8\) hollow microspheres during the process of electrochemical energy storage, \( b \)-value is calculated based on the CV curves. To obtain \( b \)-value, log\( i \) versus log\( \nu \) is plotted from 5 to 100 mV s\(^{-1}\) for cathodic peaks and anodic peaks of the CV curves (figure 6(a)), as shown in figure S3. Clearly, the calculated \( b \)-values are 0.88 (cathodic peaks) and 0.8 (anodic peaks), which are closer to 1 rather than 0.5, indicating a more pseudocapacitive behavior involving non-diffusion-controlled process for the multi-shelled Ni\(_6\)MnO\(_8\) hollow microspheres.

Figures 6(b) and (c) exhibit the GCD curves of the Ni\(_6\)MnO\(_8\)-NS electrode at different current densities (ranging from 1 A g\(^{-1}\) to 100 A g\(^{-1}\)), performed within potential window (0–0.5 V). These charge-discharge
curves display good platforms in the diagrams at different current densities. For comparison, the GCD curves of Ni$_6$MnO$_8$-NP sample were also measured at the same current densities (Supporting Information, figure S4). It can be found that the Ni$_6$MnO$_8$-NS sample exhibits much longer discharge time than the Ni$_6$MnO$_8$-NP sample. The reason is that the Ni$_6$MnO$_8$-NS sample has unique multi-shelled hollow structure with nanosheet surfaces, which endows the Ni$_6$MnO$_8$-NS hollow microsphere material with large specific surface area and abundant diffusion channels for electrolyze, thus facilitating sufficient active sites for fast faradaic reaction.

To evaluate the rate capability, the specific capacitance of the two Ni$_6$MnO$_8$ hollow samples at different current densities is calculated by equation (1) based on discharge time of the GCD curves (figure 6(d)). The results demonstrate that the Ni$_6$MnO$_8$-NS electrode displays remarkable specific capacitances of 1380, 1285, 1211, 1148, 1080, 1024, 940 F g$^{-1}$ at 1, 2, 5, 10, 20, 40, 60 and 100 A g$^{-1}$, respectively. Importantly, even at ultrahigh current density of 100 A g$^{-1}$, it still achieves 68% capacitance retention rate at 1 A g$^{-1}$. whereas, for the Ni$_6$MnO$_8$-NP electrode, the specific capacitances are much lower at the same current densities, with 882, 831, 762, 710, 664, 632, 600 and 580 F g$^{-1}$ at 1, 2, 5, 10, 20, 40, 60 and 100 A g$^{-1}$, respectively. It is worth mentioning that, although the Ni$_6$MnO$_8$-NP electrode is inferior to the Ni$_6$MnO$_8$-NS electrode in specific capacitance, its rate property is also fairly good, with 65% capacitance retention at 100 A g$^{-1}$. The cycling life of the electrode is assessed by the repeated GCD test at a successive 10 A g$^{-1}$ current density (figure 6(e)), the results indicate that both Ni$_6$MnO$_8$-NS and Ni$_6$MnO$_8$-NP samples display excellent cycle performance, and after 5000 cycles their retention ratios are 98% and 91%, respectively. Considering the charge–discharge curves is non-linear, calculation of the specific capacitance may be not accurate using equation (1), we have also calculated the specific capacity (mAh g$^{-1}$) of the Ni$_6$MnO$_8$-NS electrode using equation (S1), compared with previous specific capacitance in F g$^{-1}$, as shown in table S1. Similarly, comparison of the specific capacity (mAh g$^{-1}$) and specific capacitance (F g$^{-1}$) of the Ni$_6$MnO$_8$-NP electrode is shown in table S2.

EIS test was measured to further investigate their electrochemical behaviors, the Nyquist plots is displayed in figure 6(f). The semicircular diameter of electrodes in high frequency region indicates charge-transfer resistance ($R_{ct}$). It is distinct that $R_{ct}$ of Ni$_6$MnO$_8$-NS electrode is smaller than that of its counterpart in the Nyquist plots, manifesting Ni$_6$MnO$_8$-NS electrode has lower charge impedance. The straight linear slope of electrodes in low frequency region reveals the Warburg resistance ($R_w$) and ideal supercapacitors have the impedance curve perpendicular to the x-axis in low frequency region. Obviously, the Ni$_6$MnO$_8$-NS electrode possesses lower $R_w$ in comparison with the Ni$_6$MnO$_8$-NP electrode because of its steeper slope, so the former is much closer to ideal supercapacitors than the latter.

Compared with conventional supercapacitors, the asymmetric capacitor has the advantages of both battery-type capacitor and electrochemical double layer capacitor (EDLC) [42]. Moreover, it has high energy density and power density [43]. For further evaluating the possibility of the Ni$_6$MnO$_8$-NS electrode for practical application, a two–electrode asymmetric capacitor (ASC) was assembled with the Ni$_6$MnO$_8$-NS material and active carbon (AC) (represented as Ni$_6$MnO$_8$-NS//AC). The CV curves of AC electrode have near rectangular shape and the GCD curves show linear profile (figure S5), which display obvious EDLC behavior. In order to seek supreme voltage window under stable conditions, we tested the CV curves (figure S6(a)) at a scan rate of 20 mV s$^{-1}$ and the GCD curves (figure S6(b)) of the Ni$_6$MnO$_8$-NS//AC device at different potential windows ranging from 0–0.8 V to 0–1.5 V, which tested at a current density of 2 A g$^{-1}$. Figure 7(a) presents the CV curves carried out at various sweep rates in the operating voltage of 1.5 V which is the ultimate voltage at steady state. The GCD curves of Ni$_6$MnO$_8$-NS//AC device at different current density (1, 2, 5, 8 and 10 A g$^{-1}$) are shown in figure 7(b). Besides, the GCD curves of the ASC device show nonlinear profile, implying the contribution from Faradaic-type property of Ni$_6$MnO$_8$-NS//AC. The Nyquist plots of Ni$_6$MnO$_8$-NS//AC is displayed in figure 7(c), the lower charge impedance and the facilitated mass transfer of the electrolyte are explained by the small diameter in high frequency and the great slope in low frequency, respectively. Figure 7(d) displays the specific capacitances of 101.67, 93.87, 76.67, 66.67 and 61.33 F g$^{-1}$ at 1, 2, 5, 8 and 10 A g$^{-1}$, respectively. The Ni$_6$MnO$_8$-NS//AC device exhibits distinguished cycle performance, with a high retention rate of 93% even after 10000 charge/discharge cycles at a current density of 10 A g$^{-1}$ (figure 7(e)). The Ragone plot in figure 7(f) displays that the Ni$_6$MnO$_8$-NS//AC device can achieve a high energy density of 31.8 Wh kg$^{-1}$ at a power density of 750 W kg$^{-1}$, and still retains an energy density of 19.2 Wh kg$^{-1}$ even at high power density of 7500 W kg$^{-1}$. The energy density and power density of the Ni$_6$MnO$_8$-NS//AC device are comparable or even superior to those of some recently reported BTMOS hybrid or asymmetric supercapacitors, as shown in table S3. It indicates a promising prospect in practical applications of the Ni$_6$MnO$_8$-NS//AC device. Considering the charge–discharge curves is non-linear (figure 7(b)), the calculated energy density and power density may not be accurate using the equations (2) and (3) for supercapacitor. In comparison, we also calculated the specific energy (Wh kg$^{-1}$) and the specific power (W kg$^{-1}$) using the equations (S2) and (S3) for supercapattery, respectively. The specific energy of Ni$_6$MnO$_8$-NS//AC device is 34.9 Wh kg$^{-1}$ at a specific power of 792 W kg$^{-1}$, and the specific energy is 19.0 Wh kg$^{-1}$ when specific power is 7416 W kg$^{-1}$. It can be seen that the calculated results differ little from the
energy density and power density calculated by equations (2) and (3). Table S4 lists the detailed comparison of the obtained two parallel data based on supercapacitor and supercapattery equations, respectively.

4. Conclusions

To sum up, triple-shelled Ni₆MnO₈ hollow microspheres with nanosheet shells (Ni₆MnO₈-NS) and triple-shelled Ni₆MnO₈ hollow microspheres with nanoparticle shells (Ni₆MnO₈-NP) have been successfully synthesized through step by step adsorption and one-step adsorption of Ni and Mn ions on carbon microspheres, respectively. The as-synthesized Ni₆MnO₈-NS sample demonstrates a high specific capacitance of 1380 F g⁻¹ at current density of 1 A g⁻¹, with a high capacity retention rate of 98% after 5000 cycles at 10 A g⁻¹. The two-electrode asymmetric capacitor constructed with Ni₆MnO₈-NS//AC presents a high energy density (31.8 W h kg⁻¹ at 750 W kg⁻¹), with only 7% of cycle life loss after 10,000 repetitious charge-discharge times. Except for the good intrinsic supercapacitive property, the Ni₆MnO₈-NS sample exhibits excellent supercapacitive performance largely due to its unique multi-shelled hollow structure with plentiful nanosheets on the surfaces, which render it with large specific surface area and abundant active sites for faradaic reaction. In addition, its large pore volume and mesoporous structure with appropriate pore size can make rich diffusion channels for rapid electrolyte motion, which is superior to that of the Ni₆MnO₈-NP counterpart. The presented step by step adsorption strategy for preparing multi-shelled hollow spheres of binary transition metal oxides

Figure 7. Capacitance performance of the Ni₆MnO₈-NS//AC asymmetric capacitor: (a) CV curves at various scan rates, (b) GCD curves at different current densities, (c) EIS curve, (d) Rate capability, (e) Cyclic stability at a current density of 10 A g⁻¹, (f) Ragone plot.
provides a new approach to material structure design towards its promising application in energy conversion and storage.

Acknowledgments

We gratefully acknowledge the financial supports from the National Natural Science Foundation of China (NSFC 91834301, 21808046 and 21908037) and Anhui Provincial Science and Technology Department Foundation (201903a05020021).

ORCID iDs

Weixin Zhang https://orcid.org/0000-0001-6979-8901

References

[1] Guo J, Yin Z H, Zang X X, Dai Z Y, Zhang Y Z, Huang W and Dong X C 2017 Facile one-pot synthesis of NiCo2O4 hollow spheres with controllable number of shells for high-performance supercapacitors Nano Res. 10 405–14
[2] Wang J Y, Tang H J, Ren H, Yu R B, Qij, Mao D, Zhao H J and Wang D 2014 pH-regulated synthesis of multi-shelled manganese oxide hollow microspheres as supercapacitor electrodes using carbonaceous microspheres as templates Adv. Sci. 11 400011
[3] Mohamed S G, Hussain I and Shim J J 2018 One-step synthesis of hollow C-NiCo2S4 nanostructures for high-performance supercapacitor electrodes Nanoscale 10 6620–8
[4] Liu T, Zhang L, You W T and Yu J 2018 Core–shell nitrogen-doped carbon hollow spheres/Co3O4 nanosheets as advanced electrode for high-performance supercapacitor Small 14 1702407
[5] Zhao Y Y, Zhang P, Fu W B, Ma X W, Zhou Y, Zhang X J, Li L, Xie E Q and Pan X J 2017 Understanding the role of Co3O4 on stability between active hierarchies and scaffolds: an insight into NiMnO4 composites for supercapacitors Appl. Surf. Sci. 416 160–7
[6] Wang G P, Zhang L and Zhang J J 2012 A review of electrode materials for electrochemical supercapacitors Chem. Soc. Rev. 41 797–828
[7] Yang Z H, Xu F F, Zhang W X, Mei Z S, Pei B and Zhu X 2014 Controllable preparation of multishelled NiO hollow nanospheres via layer-by-layer self-assembly for supercapacitor application J. Power Sources 246 24–31
[8] Ji S, Ma Y Y, Wang H, Key J, Brett D J and Wang K 2016 Cage-like MnO2–Mn2O3 hollow spheres, with high specific capacitance and high rate capability as supercapacitor material Electrochim. Acta 219 540–6
[9] Shao Z M, Fang X M, Liu X Y, Yang Z H, Wang L, Chen Z X and Zhang W X 2018 Hierarchical micro-/nanostructured WO3 with structural water for high-performance pseudocapacitors J. Alloys Compd. 765 489–96
[10] Shen L F, Yu L, Yu X Y, Zhang X G and Lou X W 2015 Self-templated formation of uniform NiCo2O4 hollow spheres with complex interior structures for lithium-ion batteries and supercapacitors Angew. Chem. Int. Ed. 54 1868–72
[11] Li G, Li W, Xu K, Zou R, Chen Z and Hu J 2014 Sponge-like NiCo2O4/MnO2 ultrathin nanoflakes for supercapacitor with high-rate performance and ultra-long cycle life J. Mater. Chem. A 2 7738–41
[12] Brezesinski T, Wang J, Tolbert S H and Dunn B 2010 Ordered mesoporous alpha-MoO3 with iso-oriented nanocrystalline walls for thin-film pseudocapacitors Nature Mater. 9 146–51
[13] Zhang Y, Li L, Su H, Huang W and Dong X 2015 Binary metal oxide: advanced energy storage materials in supercapacitors J. Mater. Chem. A 3 13–59
[14] Song X X, Huang G, Qin Y, Li H and Chen H C 2018 Hierarchical hollow, sea-urchin-like and porous Ni2–xCoO2Se2 as advanced battery material for hybrid supercapacitors J. Mater. Chem. A 6 16205–12
[15] Ray A, Roy A, Ghosh M, Ramos-Ramon J A, Saha S, Pal U, Bhattacharyad S K and Das S 2019 Study on charge storage mechanism in working electrodes fabricated by sol-gel derived spindel NiMn2O4 nanoparticles for supercapacitor application Appl. Surf. Sci. 463 513–25
[16] Luo D et al 2017 Tuning shell numbers of transition metal oxide hollow microspheres toward durable and superior lithium storage ACS Nano 11 11521–30
[17] Zhao X X, Yu R B, Tang H J, Mao D, Qij, Wang B, Zhang Y, Zhao H J, Hu W P and Wang D 2017 Formation of septuple-shelled (Co3O4)12(Mn2O3)3(Co3O4)12(Mn2O3)3 hollow spheres as electrode material for alkaline rechargeable battery Adv. Mater. 29 1700350
[18] Qi L et al 2015 Multi-shelled hollow micro-/nanostructures Chem. Soc. Rev. 44 6749–73
[19] Meher S K, Justin P and Ranga Rao G 2011 Microwave-mediated synthesis for improved morphology and pseudocapacitance performance of nickel oxide ACS Appl. Mater. Inter. 3 2063–73
[20] Zhao X X, Wang J Y, Yu R B and Wang D 2018 Construction of multishelled binary metal oxides via coabsorption of positive and negative ions as a superior cathode for sodium-ion batteries J. Am. Chem. Soc. 140 17114–9
[21] Lai X Y, Halfperty E X and Wang D 2012 Recent advances in micro-/nano-structured hollow spheres for energy applications: From simple to complex systems Energy Environ. Sci. 5 5604–18
[22] Yu L, Hu H, Wu H B and Lou X W 2017 Complex hollow nanostructures: synthesis and energy-related applications Adv. Mater. 29 1604501
[23] Zhang G Q and Lou X W 2014 General synthesis of multi-shelled mixed metal oxide hollow spheres with superior lithium storage properties Angew. Chem. Int. Ed. 53 9041–4
[24] Wong Y J, Zhu L, Teo W S, Tan Y W, Yang Y, Wang C and Chen H 2011 Revisiting the Stöber method: inhomogeneity in silica shells J. Am. Chem. Soc. 133 11423–5
[25] Ren H and Yu R B 2019 Hollow multi-shelled structures for energy conversion and storage applications Inorg. Chem. Front. 6 2239–59
[26] Zhu Y R, Wang J F, Wu Z B, Jing M J, Hou H S, Jia X N and X J B 2015 An electrochemical exploration of hollow NiCo2O4 submicrospheres and its capacitive performances J. Power Sources 287 307–13
[27] Ensafi A, Moosavifard S E, Rezaei B and Kaverlavani S K 2018 Engineering onion-like nanoporous CuCo2O4 hollow spheres derived from bimetal–organic frameworks for high-performance asymmetric supercapacitor J. Mater. Chem. A 6 10497–506
Mao D, Wan J W, Wang J Y and Wang D 2019 Sequential templating approach: a groundbreaking strategy to create hollow multishelled structures. *Adv. Mater.* 31 1802874

Wang J Y, Wan J W and Wang D 2019 Hollow multishelled structures for promising applications: understanding the structure–performance correlation. *Acc. Chem. Res.* 52 2169–78

Tang C J, Liu Y N, Xu C, Zhu J X, Wei X J, Zhou L, He L, Yang W and Mai J Q 2018 Ultrafine nickel-nanoparticle-enabled SiO2 hierarchical hollow spheres for high-performance lithium storage. *Adv. Funct. Mater.* 28 1704561

Lou X W, Li C M and Archer L A 2009 Designed synthesis of coaxial SnO2@carbon hollow nanospheres for highly reversible lithium storage. *Adv. Mater.* 21 2536–9

Wang J Y et al 2016 Multi-shelled metal oxides prepared via an anion-adsorption mechanism for lithium-ion batteries. *Nat. Energy* 1 16050

Lv H P, Yuan Y, Xu Q, Liu H, Wang Y G and Xia Y 2018 Carbon quantum dots anchoring MnO2/graphene aerogel exhibits excellent performance as electrode materials for supercapacitor. *J. Power Sources* 398 167–74

Yang Z H, Lu J B, Bian D C, Zhang W X, Yang X N, Xia J F, Chen G D, Gu H Y and Ma G 2014 Stepwise co-precipitation to synthesize LiNi0.5Co0.2Mn0.3O2 one-dimensional hierarchical structure for lithium ion batteries. *J. Power Sources* 272 144–51

Ma G et al 2016 A general and mild approach to controllable preparation of manganese-based micro- and nanostructured bars for high performance lithium-ion batteries. *Angew. Chem. Int. Ed.* 55 3667–71

Li K, Luo X G, Lin X Y, Qi F W and Wu P 2014 Novel NiCoMnO4 thermocatalyst for low-temperature catalytic degradation of methylene blue. *J. Mol. Catal. A: Chem.* 383 1–9

Li L, Hu H L and Ding S J 2018 Facile synthesis of ultrathin and perpendicular NiMn2O4 nanosheets on reduced graphene oxide as advanced electrodes for supercapacitors. *Inorg. Chem. Front.* 5 1714–20

Moosavifard S E, El-Kady M F, Rahmaniifar M S, Kaner R B and Mousavi M F 2015 Designing 3D highly ordered nanoporous CuO electrodes for high-performance asymmetric supercapacitors. *ACS Appl. Mater. Inter.* 7 4851–60

Li X C, Wang L, Shi J H, Du N X and He G H 2016 Multishelled nickel-cobalt oxide hollow microspheres with optimized compositions and shell porosity for high-performance pseudocapacitors. *ACS Appl. Mater. Inter.* 8 17276–83

Guan B Y, Kushima A, Yu L, Li S, Li J and Lou X W 2017 Coordination polymers derived general synthesis of multishelled mixed metal-oxide particles for hybrid supercapacitors. *Adv. Mater.* 29 1605902

Wang Y P, Pan A Q, Zhang Y F, Shi J R, Lin J D, Liang S Q and Cao G Z 2018 Heterogeneous NiS/NiO multi-shelled hollow microspheres with enhanced electrochemical performances for hybrid-type asymmetric supercapacitors. *J. Mater. Chem. A* 6 9153–60

Gao L B, Cao K, Zhang H T, Li P F, Song J, Surjadi J U, Li Y F, Sun D and Lu Y 2017 Rationally designed nickel oxide ravines@iron cobalt-hydroxides with largely enhanced capacitive performance for asymmetric supercapacitors. *J. Mater. Chem. A* 5 16944–52