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3D sponge-like porous structure of Mn_2O_3 tiny nanosheets coated on $Ni(OH)_2/Mn_2O_3$ nanosheet arrays for quasi-solid-state asymmetric supercapacitors with high performance

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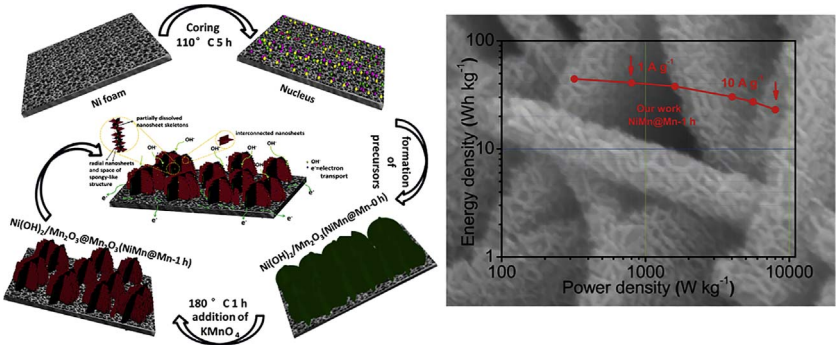
HIGHLIGHTS

- Sponge-like porous structure of Mn_2O_3 nanosheets grown on $Ni(OH)_2/Mn_2O_3$ nanosheets was prepared.
- The new strategy for preparing the composites is facile and cost-efficient.
- The structure shows superior specific capacitance and cycling life performances.
- Quasi-solid-state asymmetric supercapacitor delivers excellent energy density.

GRAPHICAL ABSTRACT

A novel 3D sponge-like porous NiMn@Mn-1 h with open channel towards electrolyte prepared via two-step grown Mn_2O_3 takes on an outstanding electrochemical performances.



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ABSTRACT

Herein, the perfect 3D sponge-like porous structure of Mn_2O_3 tiny nanosheets grown on $Ni(OH)_2/Mn_2O_3$ nanosheet arrays was successfully manufactured in situ on conductive Ni foam substrate (NiMn@Mn-1 h) by a cost-efficient and facile two-step hydrothermal method. This method included first step to synthesize $Ni(OH)_2/Mn_2O_3$ on Ni foam and second step to regrow Mn_2O_3 nanosheets on $Ni(OH)_2/Mn_2O_3$ skeletons at a higher temperature. The synergy of $Ni(OH)_2$-Mn_2O_3 and its 3D sponge-like porous morphology that is composed of tiny interconnected radial nanosheets have greatly improved conduction of electron in electrode materials and the contact area of the active materials and electrolyte. Meanwhile, the structure that possesses open channel towards electrolyte also could provide convenient access of electrolyte, promoting release of the intercalation/deintercalation pressure of electrolyte ions. Therefore, the novel sponge-like NiMn@Mn-1 h takes on an outstanding specific capacitance of 2274.4 F g^{-1} at a current density of 1 A g^{-1}. And an impressive cycle stability of 87% at 5 A g^{-1} over 10,000 cycles is also shown, which mainly benefits from the protection of external Mn_2O_3 nanosheets prepared by second step hydrothermal method. Further, the assembled NiMn@Mn-1 h//active carbon (AC) quasi-solid-state asymmetric supercapacitor (ASC) also displays a great specific capacitance (117.1 F g^{-1} at 1 A g^{-1}), an excellent cyclic stability (83% after 10,000 cycles) and a high energy density of 41.6 W h kg^{-1}. So NiMn@Mn-1 h could be one of the potential materials for application of energy storage devices.

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1. Introduction

Supercapacitors have caused widespread concern in academia and industry because of fast charge and discharge, excellent circulation performance and high power density in comparison to batteries and fuel cells [1–5]. So far, electrode materials applied to supercapacitors mainly include carbon materials [6], transitional metal oxides/hydroxides [7] and conducting polymers [8,9]. Compared to the other two, energy densities and specific capacitances of transitional metal oxides/hydroxides are higher due to fast, reversible faradaic reactions [10,11].

Ni-based oxides/hydroxides are one of the widely studied electrode materials due to high theoretical capacitance [2] and environmental friendliness [12,13]. Recently, Kim's context [14] described $Ni(OH)_2$ with porous gold as a 3D current collector, and it possessed a high volumetric capacitance of 2223 F cm^{-3} at current density of 5 A g^{-1}, but referring to high cost (golden current collectors). In addition, 3D NiAl double hydroxide/multi-walled carbon nanotube/Ni foam prepared by a three-step synthesis method was studied by Wang and his co-operators [15], which exhibited a specific capacitance of 1293 F g^{-1} at 5 mA cm^{-2} and retained the capacitance value of 83% at 30 mA cm^{-2} after 1000 cycles, but involving multi-steps and low cycle stability. In Ye's context [2], a ultrathin sheet-like Ni/Co hydroxide on a Ni foam substrate with a high specific capacitance was demonstrated; however the samples possessed a little mass loading (1.1 mg cm^{-2}) and a low cycling stability (only 77% retention at 10 A g^{-1} after 1500 cycles). Generally speaking, various defects such as high cost, complex processes and low cycle stability in these electrode materials hinder the practical application for the energy conversion and storage devices. To make up for the these defects, one promising approach realizing the practical application of electrode materials is to achieve preparation of MnNi-based oxides and hydroxides, in view of low cost, stable circulation, abundant sources and high theoretical capacitance of MnNi-based oxides and hydroxides [2,16,17]. In general, many of the current studies remain on the combination of MnO_2 and Ni-based materials, such as MnO_2-coated Ni nanorods [18], $Ni(OH)_2$-MnO_2-RGO [19], Ni@PPy@MnO_2 [20], $Ni(OH)_2$-MnO_2 [10]. However, the other valence states of manganese including MnO, Mn_2O_3 and Mn_3O_4 also have many advantages [11,21-25], particularly, Mn_2O_3 possessing the high theoretical capacitance of 1219.2 F g^{-1} at 0.5 V and nontoxicity. However, there are very few studies on combining them with $Ni(OH)_2$. In addition, although MnNi-based oxides and hydroxides have a high specific capacitance, the capacitance value of the actual samples is much smaller than that of the theoretical capacitance, which is greatly affected by the structure. As is well known, bulk materials exist the dead volume with the high mass loading and little active sites, causing a decrease in aspect of the specific capacitance [16,26]. Therefore, it is critical to devise a novel nanostructure possessing the large specific surface area and highly open porous channel towards electrolyte to improve the utilization of electrode materials. Unfortunately, to our best knowledge, the nanostructure based on $Ni(OH)_2$-Mn_2O_3 with large specific surface area and open channel for supercapacitors has been rarely reported. That is chiefly on account of the trouble in using the low cost and facile hydrothermal method to achieve the control of phase (such as Mn_2O_3) and micro morphology (such as thickness of nanosheets and porosity).

Herein, we report a cost-efficient and facile hydrothermal method to achieve formation of the 3D interconnected radial NiMn@Mn-1 h nanosheet arrays: first step hydrothermal method to synthesize large Ni $(OH)_2/Mn_2O_3$ nanosheets (NiMn@Mn-0 h) on Ni foam and second step hydrothermal method to regrow Mn_2O_3 nanosheets on NiMn@Mn-0 h skeletons at a higher temperature, in which the NiMn@Mn-1 h is completely composed of tiny interconnected radial nanosheets, forming sponge-like porous structure. In the meanwhile, we study the effect of the second-step reaction time on the morphologies and properties of the electrode materials. And in this paper, the method mainly has the following advantages: (1) the active materials solidly and directly grown on the Ni foam substrate, which eliminated the use of the conductive agent and the binder. Thus, the method could enhance the conductivity of the active materials and the effective content of the active materials in the electrodes [27]; (2) the 3D sponge-like structure possesses the structural features of open channel that make the electrolyte easily penetrate into the interior of the electrode and large specific surface area that increases active sites. Besides, this structure also has sufficient space among the nanosheets that can easily relieve the intercalation/deintercalation pressure of electrolyte ions [28]. In addition, formation of external nanosheets can also protect the internal structure from collapse; (3) Ni foams with the 3D channel structure guarantee complete contact of electrolyte and active materials. They, as current collectors, also take on excellent electrical conductivity; (4) the additive surfactant hexadecyl trimethyl ammonium bromide (CTAB) can stabilize the exposed surface [29,30] of the nanosheets, thus, inhibiting the thickening of the nanosheets. In addition, CTAB also can improve the wettability of the active materials [31], which improves the interaction between the active materials and the electrolytes; (5) synergy of Mn_2O_3 rarely reported and $Ni(OH)_2$ grown on high conductive Ni foam substrate improves conductivity of Mn_2O_3 and $Ni(OH)_2$, presenting a low charge transfer resistance and a high specific capacitance.

Therefore, the NiMn@Mn-1 h displays the specific capacitance of 2274.4 F g^{-1} at a current density of 1 A g^{-1}. Besides, compared to precursors, the capacitance retention rate of NiMn@Mn-1 h is improved by 11% at 10 A g^{-1}. And a high cyclic stability (capacitance of 87% remained at 5 A g^{-1} over 10,000 cycles) is also shown. Furthermore, in comparison with the electrolyte of water system, it is found that the devices assembled with quasi-solid-state electrolyte have many advantages: convenient to carry, safety, stabilization and small and ultrathin shape [32–35]. Thus, polyvinyl alcohol (PVA)/KOH electrolyte was employed in the assembled process to better suit to the application of practical production and life. The NiMn@Mn-1 h//AC assembled into ASC possesses an excellent specific capacitances of 117.1 F g^{-1} at a current density of 1 A g^{-1}, an appropriate capacitance retention rate of 55% at 10 A g^{-1}, a great cyclic stability (83% of the original capacitance at 5 A g^{-1} after 10,000 cycles) and a high energy density of 41.6 W h kg^{-1} at a power density of 799.4 W kg^{-1} (even the power density is up to 7996.2 W kg^{-1}, energy density still could be 23.14 W h kg^{-1}). The all results make NiMn@Mn-1 h//AC be a great potential material for the energy conversion and storage devices.

2. Results and discussion

2.1. Characterization of morphology and composition

In the paper, the formation process for the spongy-like NiMn@Mn-1 h nanosheets is presented in Scheme 1. Firstly, the Ni^{2+} reacts with the OH^- generated from weak reaction of NO_3^- of reactants: $4CH_3CH_2OH + NO_3^- \rightarrow 4CH_3CHO + NH_3\uparrow + OH^- + 2H_2O$ and the hydrolysis of the cation, forming $Ni(OH)_2$ nucleus and further growing into primary particles at hydrothermal process of 110 °C. Due to the greater solubility value (K_{sp}) of $Mn(OH)_2$ than that of $Ni(OH)_2$, $Mn(OH)_2$ is generated along with more OH^- [10]. Then, $Mn(OH)_2$ is transformed into MnO_2 by following oxidation reactions. Because of the reducing action of ethanol at low temperature (110 °C) hydrothermal process, the MnO_2 is further reduced into Mn_2O_3 as follows: $2MnO_2 + CH_3CH_2OH \rightarrow Mn_2O_3 + CH_3CHO + H_2O$ [36]. These $Ni(OH)_2$ and Mn_2O_3 primary particles are further polymerized and crystallized into large cross-linked nanosheets, where these Mn_2O_3 are embedded into the large nanosheets skeleton. In addition, the interaction between ion head from the CTAB molecules and OH^- can stabilize the surface of the nanosheets, preventing nanosheets from thickening. In the second process of the reaction (180 °C for 1 h), the $KMnO_4$ as the manganese source, redundant CTAB as the reductant and large NiMn@Mn-0 h nanosheet as nucleation site produce Mn^{3+} as the nucleus [37], ultimately growing into this external tiny Mn_2O_3 nanosheets with large