Fabrication of MnSn(OH)$_6$@MoS$_2$ Core-Shell Nanostructure with Excellent Supercapacitive Performance

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Abstract. Three-dimensional (3D) core-shell structure of MnSn(OH)$_6$ nanobox with MoS$_2$ nanosheet is grown by series of simple steps for supercapacitor application. This core-shell is composited of MnSn(OH)$_6$ nanobox as core and MoS$_2$ nanosheet as shell. As-synthesized electrode material was characterized by Field emission scanning electron microscope (FESEM), energy dispersive spectroscopy (EDS) and transmission electron microscope (TEM). As-fabricated MnSn(OH)$_6$@MoS$_2$ electrode exhibited redox behavior with excellent specific capacitance of 1176 F g$^{-1}$ at a current density of 4 A cm$^{-2}$. These findings make MnSn(OH)$_6$@MoS$_2$ a better alternative source for energy storage devices.

Keywords: Supercapacitor, MnSn(OH)$_6$, Nanoboxes, MoS$_2$, Core-shell, Nanosheets.

1. Introduction

For the new generation of energy-storage devices, supercapacitors (SCs) are very promising because of their longer cycling life, rapid charge/discharge and high power density. However, their lower energy density limits their potential application in energy storage devices [1]. Recently, binary metal oxides with spinel structure have received great interest due to their low cost, environmentally friendliness and high performance in many energy storage applications such as Li-ion batteries and supercapacitors [2]. So far many research groups have been developed different metal oxide stannates such as Co$_2$SnO$_4$, Zn$_2$SnO$_4$, Ca$_2$SnO$_4$, Mn$_2$SnO$_4$ and Mg$_2$SnO$_4$ [3]-[7]. Among them, Mn$_2$SnO$_4$ shows a cubic spinel structure with space groupFd$ar{3}$m and these materials (Mn and Sn) are individually excellent electrochemical active materials with high capacitance for supercapacitors because of nontoxic, less expensive and natural abundance. What’s more, transition metal sulfides like MoS$_2$ possesses high chemical stability, mild toxicity, wide potential window and high storage capacity which make it an attracted electrode material for supercapacitor. Herein, we report three dimensional core-shell structure of MnSn(OH)$_6$@MoS$_2$ synthesized by an easy chemical route for the application of supercapacitor. This core-shell is composited of MnSn(OH)$_6$ nanobox as core and MoS$_2$ nanosheet as shell. The synergistic effect between them can improve supercapacitive performance of the electrode further by increasing the porosity, electric conductivity and operating potential range.
2. Experimental part

All reagents are of analytical grade and commercially available. They were used as received without further processing.

*Synthesis of MnSn(OH)$_6$@MoS$_2$ core-shell Structures:* In a typical synthesis, 1.92g MnCl$_2$ powders and 2.844g SnCl$_2$ powders were dissolved in deionized water (300ml) and 99% ethanol (100ml), respectively, with vigorous stirring 1h. Then, the SnCl$_2$ ethanol solution was added into the MnCl$_2$ aqueous solution with stirring for 1h. After that, 50ml NaOH aqueous solution (4M) was added into the above mixed solution with stirring for another 0.5h. The pink products were collected by centrifugation and washed with deionized water and ethanol several times, followed by drying for a whole night at 60°C. Then, the above products, 0.9197g (NH$_4$)$_6$Mo$_7$O$_{24}$$\cdot$4H$_2$O and 3g thiourea were dissolved into 100mL of deionized water and the solution was kept at 180°C for 24 h. Next, the autoclave was cooled naturally and MnSn(OH)$_6$@MoS$_2$ sample was finally collected and cleaned by deionized water for several times, followed by drying at 50°C overnight.

*Characterization and Electrochemical Measurements:* As-synthesized sample was characterized by Field Emission Scanning Electron Microscope (FESEM), Transmission Electron Microscope (TEM) and electrochemical measurements. The CV analysis of electrochemical test was measured at various scan rates over a voltage range of -1–0 V. The GCD tests were performed at various current densities over a potential range of -1–0V.

3. Result and Discussion

To check the surface morphology of as-synthesized material, the sample was characterized by FESEM and the images are shown in Fig. 1. From Fig. 1 (a), it is clear that as-synthesize MnSn(OH)$_6$ material shows the pretty uniform and beautiful morphology of 3D nanoboxes. Further, the high-resolution image of MnSn(OH)$_6$@MoS$_2$ is shown in Fig. 1 (b) which confirms that the 3D nanoboxes are covered by ultrathin 2D nanosheets. This type of architecture is beneficial to obtain the high surface area which enhances the electrochemical performance of the material. Further, EDS element analysis results of MnSn(OH)$_6$ and MnSn(OH)$_6$@MoS$_2$ are shown in Fig. 1 (c-d). From Fig. 1 (c-d), it can be observed that the contrast of Mn is equivalent to the contrast of Sn which confirms the successful synthesis of MnSn(OH)$_6$ nanoboxes. And both the element Mo and S presented in image also confirms the successful synthesis of MoS$_2$ nanosheets. The appearance of Na is probably the residue of NaOH during the experiment part.
Figure 1. (a) FESEM images of MnSn(OH)$_6$ nanoboxes. (b) FESEM images of MnSn(OH)$_6$@MoS$_2$ composites. (c-d) corresponding EDS results.

For detailed morphology evolution of as-synthesized MnSn(OH)$_6$@MoS$_2$ nanoboxes, the sample was characterized by TEM and the images are shown in Fig. 2. Fig. 2(a) shows the pretty uniform and beautiful morphology of the cubical shapes. From Fig. 2(b), it can be observed that 3D MnSn(OH)$_6$ nanoboxes are covered by ultrathin 2D ultrathin transparent nanosheets. This ultrathin morphology is beneficial to improve the electrochemical performance by providing larger contact area and shorter diffusion length.

Figure 2. (a) TEM patterns of as-synthesized MnSn(OH)$_6$ nanoboxes (b) TEM patterns of MnSn(OH)$_6$@MoS$_2$ composites.

To explore the electrochemical properties of MnSn(OH)$_6$@MoS$_2$ electrode for the application in supercapacitor, the MnSn(OH)$_6$@MoS$_2$ electrode was tested as the working electrode using a three-electrode system in 0.5M Na$_2$SO$_4$ electrolyte. Fig. 3(a) shows the CV curves of MnSn(OH)$_6$@MoS$_2$ electrode recorded at various scan rates for the potential range from -0.8 to 0.1 V. Further, all the CV curves exhibit a pair of redox peaks that demonstrate the strong pseudocapacitive behavior of MnSn(OH)$_6$@MoS$_2$. As the scan rate increases from 5 to 80 mV s$^{-1}$, the current response also increases without major change in the shape of curves which shows the improved electron transport properties of the electrode. The galvanostatic charge/discharge (GCD) curve recorded at various
current densities from 4 to 16 mA cm$^{-2}$ is shown in Fig. 3 (b-c). The shape of curves retains at higher current density also which signifies the high rate capability of the electrode material. The MnSn(OH)$_6$@MoS$_2$ electrode exhibited excellent specific capacitance of 1176 F g$^{-1}$ at a current density of 4 A cm$^2$, while the pure MnSn(OH)$_6$ electrode showed specific capacitance of only 53 F g$^{-1}$ at a current density of 4 A cm$^2$. Such an excellent capacitance of MnSn(OH)$_6$@MoS$_2$ is achieved because of the smartly designed 3D nanoflowers. These results are best in terms of capacitance and cycling stability among recently published studies and indicate the potential use of as-fabricated MnSn(OH)$_6$@MoS$_2$ electrode in the next generation of energy-storage devices.

![Figure 3](image)

**Figure 3.** (a) CV curves of MnSn(OH)$_6$@MoS$_2$ electrode at various scan rates (b) GCD curves of MnSn(OH)$_6$ electrode at various current densities (c) GCD curves of MnSn(OH)$_6$@MoS$_2$ electrode at various current densities.

4. **Conclusion**

In summary, MnSn(OH)$_6$@MoS$_2$ core-shell structures were successfully prepared by a simple hydrothermal method. FESEM measurements revealed that MnSn(OH)$_6$@MoS$_2$ core-shell structures possess a 3D architecture. Electrochemical test revealed that MnSn(OH)$_6$@MoS$_2$ had superior capacitive response and longer cycling life than pure MnSn(OH)$_6$. The unique design of 3D core-shell structures provides a large surface area and short pathway for ion diffusion which may be the responsible for high electrochemical performance of MnSn(OH)$_6$@MoS$_2$ electrode. This work aims to give people some inspiration, and maybe it can be also used for gas sensing.
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