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Fabrication of MnS@Ni(OH)$_2$ Composite for improved supercapacitor applications

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Abstract:

In this present study, we have fabricated the electrodes of MnS@Ni(OH)$_2$ on Ni-foam. MnS was electrodeposited by cyclic voltammetry and Ni(OH)$_2$ was electrodeposited by using chronoamperometry method. The phase purity and the presence of functional groups are confirmed by XRD and FT-IR techniques. Moreover, the nanoparticle morphology of the electrodeposited MnS and uniformly modified surface of MnS by Ni(OH)$_2$ has been recognized by SEM analysis. The reversibility and faradic nature of the electrodes were identified by cyclic voltammetry. It has delivered the higher specific capacitance of 3185 F/g at a current density of 1A/g with excellent cycle stability in the 1000th cycles. The present study strongly recommended that MnS@Ni(OH)$_2$ has a reliable electrode for the high-performance supercapacitor applications.

1. Introduction

Supercapacitor is one of the most attractive technology for the energy storage and conversion in the delayed usages in portable electronic devices and electric vehicles. Recently, transition metal sulfide was appeared as a promising material for energy storage devices due to their variety of structural types, rich electrochemical activity and higher conductivity than corresponding metal oxides. Generally, various naturally occurring metal sulfides such as FeS_2, MoS_2, Ni_3S_2 and Cu_2S have been reported for different applications such as Supercapacitor, Lithium-ion battery, sodium-ion battery, solar cells and photocatalytic applications. Among them, MnS is p-type semiconductor with wider band gap energy of 3.1 to 3.7 eV with good electronic conductivity. Theoretical specific capacitance of the MnS is 616 mAh/g, which possess the higher redox process leads to the improvement of the energy density of the electrodes. Sofor, MnS was prepared by hydrothermal method, SILAR method, chemical method and chemical bath deposition method.Nowadays, the surface modification of the metal sulfide has been done by various metal hydroxides such as Ni(OH)$_2$, Cu(OH)$_2$, Co(OH)$_2$ and NiCo(OH)$_2$. However, there is no attempt to modify the surface of MnS by Ni(OH)$_2$.Herein, the present investigation to fabricate nanoparticle MnS@Ni(OH)$_2$ thin films directly grown on Ni-foam by electrodeposition method. MnS@Ni(OH)$_2$has delivered the highspecific capacitance of 3185 F/g at a current density of 1A/g with excellent cycle stability.

2. Fabrication of materials

Manganese sulfide was electrodeposited by cyclic voltammetry method using three electrode systems in Autolab instrument (AUT72381), Ni-Foam as working electrode, Pt as Counter Electrode, Ag/AgCl as reference electrode for this process. The mass loading of the electrode material is 0.7mg.

Bare Ni(OH)$_2$ and MnS@Ni(OH)$_2$ was electrodeposited using chrono amperometry method. In a typical process, 0.05M of $NiCl_2$ $6H_2O$ and 2M of KNO_3 in 50ml used as electrolyte solution with constant potential of -0.9V for 300 seconds. The deposited electrode was rinsed with water and ethanol and dried for 60°C for 12 hours. The amount of Ni(OH)$_2$ deposited on bare and MnS electrode is 1.0 mg and 1.5 mg respectively.

3.Results and Discussion

3.1 XRD and FTIR analysis

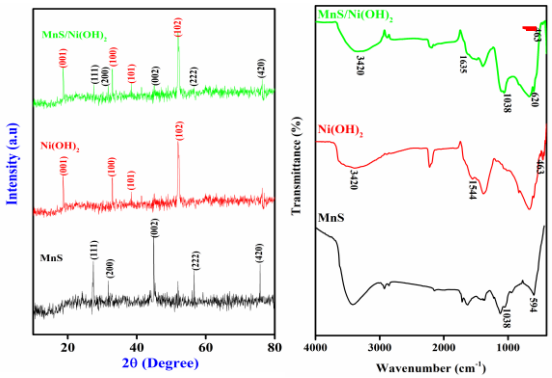

Figure.1 (a) XRD pattern and (b) FTIR spectrum of MnS, Ni(OH)$_2$ and MnS@ Ni(OH)$_2$.

Figure 1a shows the obtained XRD results of MnS, Ni(OH)$_2$ and their hybrids of MnS@Ni(OH)$_2$. XRD pattern of the electrodeposited MnS shows the diffraction peaks at (2θ) 27.45°, 30.92°, 45.57°, 54.12° with their corresponding planes values of (111), (200), (220) and (311). It is well indexed with the JCPDS File No: 040-1288 [1,2] and belongs to cubic crystal system. The XRD pattern of Ni(OH)$_2$ are well indexed with JCPDS file no: 01-1047 [3] and it belongs to hexagonal crystal system. The major diffraction peaks are 19.0°, 32.9°, 38.5° and 51.9° with their planes of (001), (100), (101) and (102) respectively.XRD results of MnS@Ni(OH)$_2$ hybrids have clearly demonstrated presence of these two phases in it. The sharp peaks of the electrodeposited materials have exhibited the good crystallinity and phase purity.

Figure 1b shows the FT-IR spectra of bare MnS, Ni(OH)$_2$ and hybrid of MnS@Ni(OH)$_2$. The peak at 592cm^{-1} is attributed to the presence of MnS[4]. The formation of the Ni(OH)$_2$ is confirmed by the presence of absorption peak at 463cm^{-1} is assigned for the stretching vibration band of Ni-O and the broad band at 3420cm^{-1} is assigned for the stretching vibrations of -OH groups in Ni(OH)$_2$ [5,6]. In the hybrid of MnS@Ni(OH)$_2$ have absorption peaks of 463cm^{-1} assigned for Ni-O, 620cm^{-1} assigned for Mn-S and the broad band at 3420cm^{-1} for -OH groups. Moreover, the broader peak at 3420cm^{-1} in Ni(OH)$_2$ and MnS@Ni(OH)$_2$ indicates the

presence of hydroxyl groups of water molecules.

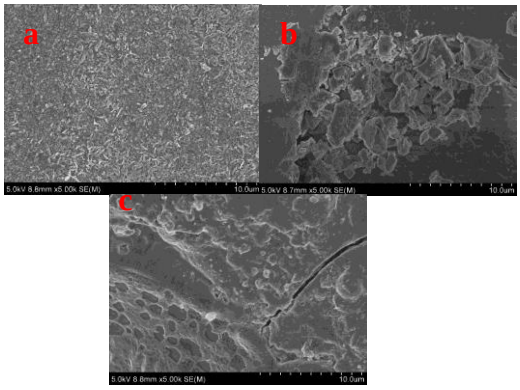

Figure.2 SEM images of (a) MnS (b) Ni(OH)$_2$ and (c) MnS@ Ni(OH)$_2$.

Figure 2a-c displays the SEM images of MnS, Ni(OH)$_2$ and MnS@Ni(OH)$_2$. SEM images of electrodeposited MnS has reveals the nanoparticle morphology, whereas the Ni(OH)$_2$ and MnS@Ni(OH)$_2$were exhibits the uniformly adhered thin film of nickel hydroxide on the surface of the Ni-Foam and MnS surface. It clearly reveals the formation of the composite hybrids of MnS@Ni(OH)$_2$.

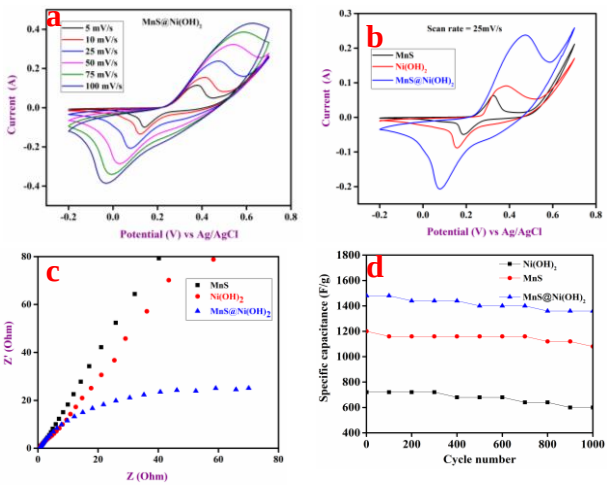

Figure.3 (a) CV curve of MnS@Ni(OH)$_2$ at different scan rates, (b) Comparison CV curve of the electrodes at 25mV/s (c) Nyquist plot of the electrodes and (d) Cycle stability of the electrodes.

CV curves in Figure 3a&b obviously explicit that, the good reversibility with strong redox behavior of the electrodes. It strongly demonstrates that, the pseudocapacitance nature of materials. EIS was analyzed to understand the kinetics of electrochemical reactions of the electrodes during the cyclic process, which is displayed in Figure 3c. The slope intercept point of Ni(OH)$_2$, MnS and MnS@Ni(OH)$_2$ in the x-axis is 0.55, 0.58 and 0.50Ω respectively, which relates to the solution resistance of the electrolyte/electrode interface.There is no more semicircle in the high frequency region corresponds to the poor charge transfer resistance. The straight line in the lower frequency indicates the good ionic conductivity of the materials.The non-linear discharge plateau of the materials clearly represents the pseudocapacitance behavior of the electrodes [7].Whenever to increase the current density from 1 to 20 A/g, the discharge specific capacitance was drastically reduced from 1100 to 720 F/g for Ni(OH)$_2$, 1848 to 1280 F/g for MnS and 3185 to 1480 F/g for hybrids of MnS@Ni(OH)$_2$, it is obtained by the improper electrochemical activity of the electrode materials when applying higher current density [8].Figure 3d shows cycle stability of Ni(OH)$_2$, MnS and MnS@Ni(OH)$_2$. The hybrid of MnS@Ni(OH)$_2$ shows the superior cycle stability of 92% of its initial capacitance in the 1000th cycle. Which is higher than the cycle stability of MnS is 90%, Ni(OH)$_2$ is 83.3% in the 1000th cycle.

3. Conclusions

The fabricated the nickel hydroxide modified MnS was prepared by electrodeposition method.The nanoparticle morphology of electrodeposited MnS and thin film of Ni(OH)$_2$ were confirmed by SEM images.CV results exposed redox behavior and the good reversibility of the electrodes. The lower solution resistance and superior ionic conductivity of the hybrid MnS@Ni(OH)$_2$ has given the better electrochemical activity of the electrodes.GCD results displayed the hybrid of MnS@Ni(OH)$_2$ is 3185 F/g at current density of 1A/g, it shows the improved cycle stability of 92% capacity retention in the 1000th cycle at maximum current density of 20A/g.This study strongly recommended that, the metal sulfides/metal hydroxide has the bright future to meet the demands in the supercapacitors.

Acknowledgements

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