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Facile Electrochemical Synthesis of Porous Manganese-Cobalt-Sulfide Based Ternary Transition Metal Sulfide Nanosheets Architectures for High Performance Energy Storage Applications

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ABSTRACT

In this study, we have reported a facile growth of ultrathin mesoporous manganese cobalt sulfide (MCS) nanosheet arrays on Ni-foam substrate by a facile electrodeposition approach for high performance supercapacitor applications. We have developed the extremely energy-saving and rapid synthetic methodologies for the growth of highly active binary transition metal sulfide. The nanosheet architectures have been characterized using the techniques such as XRD, FESEM, TEM, XPS and Raman spectroscopy to understand the growth mechanism. The high porosity, high surface area and good electrical conductivity of the MCS nanosheets arrays make it a promising electrode material for supercapacitor. MCS nanosheets exhibit a high specific capacitance of 2421 Fg^{-1} at a current density of 1 Ag^{-1} along with excellent cycling stability, demonstrating its potential as an efficient electrode material for next generation supercapacitors.

1. Introduction

To overcome the problems associated with the immeasurable expenditure of conventional non-renewable energy resources such as fossil fuels and drastically fluctuating climatic conditions, an intense desire to establish renewable and clean energy resources is highly essential. Efficient, low cost and eco-friendly energy devices like solar cells [1], fuel cells [2], battery [3] and supercapacitors [4] are vital components in the energy conversion-storage-delivery chain and have drawn growing attention in the 21st century [5]. Supercapacitors, also known as electrochemical capacitors, have drawn a great interest and considered to be the most promising candidate for next generation energy storage devices owing to their ultrahigh power density, long cycle life, wide operation temperature range, and environmental friendliness [6–8]. Typically supercapacitors are classified into two categories based upon the mechanism involved during the charge storage processes (i) electric double layer capacitor (EDLC) and (ii) pseudocapacitor. The former stores the charges via electrostatic adsorption/desorption at the electrode surface whereas in pseudocapacitors, it is due to fast faradaic redox reaction [9,10].

To date, several transition metal oxides and sulfides have been explored for supercapacitor applications due to their enhanced electrochemical properties associated with multiple oxidation states. In recent years, transition metal oxides such as Co_3O_4 [11], NiO [12], $NiCo_2O_4$ [13], $CuCo_2O_4$ [14], $MnCo_2O_4$ [15], $ZnCo_2O_4$ [16] and metal sulfides such as CoS [17], NiS [18], $NiCo_2S_4$ [19] have emerged as high performance electrode materials for supercapacitors. Recently, transition metal chalcogenides attracted much interest in the electrochemical energy storage since sulfur ions tend to create more flexible structures as compared to the oxygen ions due to higher electro negativity of sulfur thereby blocking the disintegration of the structure by the elongation between layers and making charge transportation easier [20]. The chemistry of binary metal sulfides have attracted a wide spread attention due to the higher active redox sites, as well as mechanical and thermal stability compared to that of their corresponding single component metal oxides. Among them, manganese based oxides and sulfides have attracted considerable attention owing to their eco-friendly nature and high redox reactions [21]. Manganese sulfide possesses high theoretical specific capacitance and higher electronic conductivity (as high as $3.2*10^3$ s/cm) than their oxides or hydroxides [22]. On the other hand, cobalt sulfides exhibits excellent electrochemical performance, however their rapid capacity fading over long cycles limits their applications in electrochemical energy storage devices [23,24]. Hence, metal

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sulfide comprising both manganese and cobalt can provide efficient transport rate of ions and electrons leading to remarkable electrochemical performance with higher capacitance compared to that of MnS and CoS. Mn-Co based metal oxides possess multiple oxidation states which enhance the faradic pseudo capacitive properties of the material [25]. Previously, Mondal et al. synthesized $MnCo_2O_4$ by hydrothermal method for lithium-ion batteries and supercapacitor application [26]. Li et al. reported one dimensional $MnCo_2O_4$ nanowire arrays fabricated on Ni-foam substrate by a facile hydrothermal method for electrochemical energy storage application [27]. Chen et al. have prepared one-dimensional hollow tubular structure of $M_xCo_{3-x}S_4$ for supercapacitor application [28].

In this present work, we have prepared manganese cobalt sulfide (MCS) nanosheet arrays and analyzed its electrochemical performance for the supercapacitor application. MCS nanosheet arrays are grown on Ni foam current collector by a low cost and highly reproducible electrodeposition method. Generally Ni foam provides direct electron pathways and high porosity, which make smoother electron transportation, accelerating electrolyte penetration and enhancing high surface area which are beneficial for the electrochemical performances. The growth of MCS nanosheets directly on Ni foam substrate avoids the use of polymer binders and conducting additives which might result in better mechanical adhesion and electrical contact with the current collector [29,30]. The obtained MCS nanosheets showed excellent supercapacitive performance in terms of specific capacitance, energy density and cyclic stability, which is favorable for energy storage applications.

2. Experimental

2.1. Materials

Manganese chloride tetrahydrate ($MnCl_2.4H_2O$, 98%, HIMEDIA, India), cobalt nitrate hexahydrate ($Co(NO_3)_2.6H_2O$, 97%, Merck, India), potassium chloride (KCl, Merck, India), thioacetamide (CH_3CSNH_2, 99%, alfa Aesar (UK)), potassium hydroxide (KOH, 85%, Alfa Aesar (UK)) were used as received without further purification.

2.2. Growth of $MnCo_2S_4$ (MCS) on nickel foam using electrodeposition

The MCS nanosheet arrays were directly grown on flexible Ni foam by a simple electrodeposition approach. The reaction solution was obtained by mixing 0.01 M of $MnCl_2.4H_2O$, 0.02 M of $Co(NO_3)_2.6H_2O$, 0.01 M of KCl and 0.1 M of CH_3CSNH_2 in 10 mL DI water under sonication. To study the growth mechanism of MCS samples, we have electrodeposited MCS on Ni foam at different potential using same precursors. Similarly, we also varied the concentration of precursor solution with 0.02 M of $Co(NO_3)_2.6H_2O$, 0.01 M of KCl and different concentration of $MnCl_2.4H_2O$ (0.03, 0.05 and 0.07 M) and 0.1 M of CH_3CSNH_2, yielding the MCS samples named as MCS-0.03, MCS-0.05 and MCS-0.07 respectively. Prior to electrodeposition, the Ni foam was cut into pieces and cleaned thoroughly by ultra-sonication in ethanol and DI water for 10 minutes to remove surface contaminants. For the electrodeposition of cobalt manganese sulfide (CMS), we used 0.02 M of $MnCl_2.4H_2O$, 0.01 M of $Co(NO_3)_2.6H_2O$, 0.01 M of KCl and 0.1 M of CH_3CSNH_2. For comparison, we also electrochemically deposited manganese sulfide (MnS), cobalt sulfide (CoS) and $MnCo_2O_4$ (MCO) on Ni foam substrate. For the preparation of MnS, we used 0.01 M of $MnCl_2.4H_2O$ and 0.1 M of CH_3CSNH_2. Similarly, in case of CoS synthesis, 0.01 M $Co(NO_3)_2.6H_2O$ and 0.1 M of CH_3CSNH_2 are used as precursors. For the preparation MCO nanosheets, 0.01 M $MnCl_2.4H_2O$, 0.02 M $Co(NO_3)_2.6H_2O$ and 0.01 M of KCl salt were used as precursors.

The electrodeposition of MCS nanosheet arrays was performed using PG262A potentiostat/galvanostat (Techno Science Ltd., Banglore) by chrono-amperometric technique in an electrochemical glass cell with three electrode configuration. During electrodeposition, Ni foam acts as the working electrode, Ag/AgCl as reference electrode and Pt as counter electrode. The cathodic deposition of MCS film on Ni foam substrate was performed at −1.1 V by maintaining the temperature of electrolyte solution at 70 °C at time duration of 3 minutes. After that, the electrodeposited samples were washed with DI water several times followed by vacuum drying at room temperature and then dried at 60 °C for 2 h. The MCS nanosheets are prepared with different working potentials of −1.3 V, −1.5 V, −1.7 V and −2 V during the electrodeposition process and the resulting samples are denoted as MCS-1.3, MCS-1.5, MCS-1.7 and MCS-2. Further, MCS nanosheets were prepared under various electrodepositions with dwelling time of 2 min, 5 min and 7 min, which are hereafter denoted by MCS–2 min, MCS–5 min and MCS–7 min. We also prepared MCS and CMS samples on indium tin oxide (ITO)/glass slides to check the effect of substrate and denoted them as MCS-ITO and CMS-ITO. Further, we fabricated coin cell type symmetric supercapacitor by using the MCS nanosheets electrodes on Ni foam (as electrodes) separated by PVDF membrane with 2 M KOH as the electrolyte.

2.3. Characterization

The morphology and elemental composition of the samples were analyzed using FE-SEM (MERLIN compact with GEMENI I electron column, Zeiss Pvt.Ltd, Germany) and TEM (JEOL JEM3010). XRD pattern were obtained by a Brucker D8 advanced diffractometer using Ni filtered Cu-Kα radiation (λ=1.54184 A°). Raman spectrum was measured on micro-Raman spectrometer (Horiba Scientific T64000) with a laser excitation source having a wavelength of 514 nm and laser power of 20 mW cm^{-2}. All XPS measurements were performed by VG Microtech, England (Multi-Lab, ESCA-3000. Sr. No.- 8546/1, Multi-Lab).

2.4. Evaluation of electrochemical properties

The electrochemical supercapacitor measurements for the sample were performed in a three electrode system using 2 M aqueous KOH solution as the electrolyte. The cyclic voltammetry (CV) and charge-discharge (CD) measurements were carried out at keeping the potential window fixed at 0.5 V (-0.1 V to 0.4 V) vs Ag/AgCl. The freshly prepared MCS on Ni foam substrate was used as the working electrode and Pt wire as the counter electrode. The mass loading of the MCS nanosheets deposited on Ni foam is found to be 1.5 mg and the mass loading of other active materials used for comparison is given in Table S1 (supporting Information). The specific capacitance (C_{sp}) was calculated from cyclic voltammetry curves using the following equation;

$$C_{sp} = \frac{\int I(v)dv}{ms * 2\left[V_f - V_i\right]} \ (\mathrm{Fg}^{-1}) \quad (1)$$

Where, the integral part in the numerator gives the area under the CV curve, "m" is the mass of the active material, "s" is the scan rate, and $[V_f - V_i]$ is the potential window (V_f and V_i are the final and initial potential values respectively). From the charge/discharge curves, specific capacitance of the material was calculated using the following equation:

$$C_{sp} = \frac{I}{m * \left(\frac{dV}{dt}\right)} \ (\mathrm{Fg}^{-1}) \quad (2)$$