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Design of MnS@MWCNT Nanocomposite Cathode for Ultra-high Efficient Supercapacitors

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Abstract – The aim of this study was to investigate the usability of MnS (Manganese Sulfide) nanoparticles in supercapacitor applications. MnS nanoparticles were synthesized using the microwave synthesis method. Additionally, a multi-walled carbon nanotube (MWCNT) was incorporated into the MnS structure to prepare MnS@%10MWCNT. The microwave synthesis method was chosen due to its fast, energy-efficient, and easily controllable synthesis process. The size and morphological properties of the synthesized nanoparticles were determined using analytical techniques such as X-ray diffraction (XRD) and scanning electron microscopy (SEM). The results demonstrated that the microwave-synthesized MnS nanoparticles possessed a crystalline structure and a homogeneous distribution. The incorporation of MWCNT was confirmed through SEM images and XRD analysis. Subsequently, the usability of the synthesized MnS and MnS@%10MWCNT nanoparticles in supercapacitor applications was evaluated. The supercapacitor performance was examined using electrochemical characterization methods such as cyclic voltammetry and continuous charge-discharge tests. The results of the study revealed that MnS nanoparticles exhibited high capacitance and fast charge-discharge characteristics in supercapacitor devices. Furthermore, it was observed that the capacitance and stability increased with the incorporation of MWCNT. This study demonstrates the potential of MnS and MnS@%10MWCNT nanoparticles in energy storage. The microwave-synthesized MnS and MnS@%10MWCNT nanoparticles highlight their potential in supercapacitor applications. These findings represent an important step towards the expansion of nanomaterials' utilization in energy storage and the development of more efficient supercapacitor devices.

Keywords – Mns, MWCNT, Supercapacitors, Microwave Synthesis, Energy Storage

I. INTRODUCTION

Due to globalization, the energy issue is of great importance in the last countries of the world. Energy production in the world is based on coal, natural gas, and oil. However, the energy produced in these ways is decreasing [1]. People's need for energy sources is increasing. One of these energy sources is renewable energy sources. Due to global climate change, the world should encourage the transition to renewable energy sources [2]. Solar cells are the most common renewable energy source. The development and production of solar cells are the subject of research [3]. However, energy obtained from renewable resources for secluded areas has many compensations over usual supplies, but a negative characteristic is that the source that it is stochastic in nature and subsequently difficult to regulate. To regularize an intermittent renewable energy supply, an proper energy storage component with high specific power and at the same high specific energy over periods minutes or hours is required. Today's most advanced energy storage devices are supercapacitors. Supercapacitors show different properties compared to other energy storage devices[4]. Supercapacitors have high power density. Electrochemical supercapacitors are an important tool of the electrochemical energy storage system. MnS has recently been widely used as a better electrode material in supercapacitors. The barrier to its non-commercial use is its low energy density after storage. MnS is a super-capacitive electrode material that stores energy better than various transition metal oxides [5]. Charge storage analysis of the MnS-CT electrode was performed according to the literature [6]. In this study, simple hydrothermal synthesis of MnS nanoparticles on carbon textiles was carried out. Carbon nanotubes have properties that make them of great interest in various fields. These are shown as high thermal conductivity and high field emission. Furthermore, their electrical conductivity and power density are higher compare to metal oxides. Carbon nanotubes are divided into single-walled (SWCNT) and multi-walled (MWCNT) [7]. Some material properties of carbon nanotubes were investigated [8].

Herein, MnS and 10%wt MWCNT doped MnS were synthesized via simple, low-cost and fast microwave-assisted method. Furthermore, the electrochemical features of the prepared MnS and 10%wt MWCNT doped MnS based cathodes were investigated three electrodes via a potentiostat/galvanostat system. MnS based cathode exhibited a capacitance as 3940 while 10%wt MWCNT doped MnS cathode reached to 4747.

II. Materials and Method

A. *Materials*

$Mn(NO_3)_2.4H_2O$, multi-walled carbon nanotubes (MWCNT), and Na_2S were of analytical grade and used without additional purification. All the reagents employed in the experiments were obtained from Sigma-Aldrich Co. LLC. The reactions were conducted in a customized 100 mL Teflon-lined chamber, and heating was performed using a microwave hydrothermal synthesis system (Milestone/FlexiWave Advanced Flexible Microwave Synthesis Platform).

B. *Method*

1.25 g of manganese (II) nitrate tetrahydrate was dissolved in 100 ml of de-ionized water and added 0.3 g of polyvinylpyrrolidone (PVP), finally the mixture subjected to ultrasonication process. Then, 100 ml of the mixture was divided into two 50 ml beakers. Next, 10%wt of Multi-Walled Carbon Nanotube (MWCNT) was added to one 50 ml baker and applied an ultrasonication process. After that Two mixtures were placed to Teflon autoclaves for microwave processing. A 1200 Watt microwave irradiation was applied at 180°C for 15 min. In the second step, 0.784 g of Na_2S was added to two Teflon autoclaves, separately. Moreover, pre-cleaned 1x2 (cm^2) nickel foams were placed to the autoclaves. Finally, at 180°C a 1200 Watt microwave irradiation was performed for 2 h. Next, the coated nickel foams were rinsed with deionize water and dried in an oven at 60°C for 24 h.
Furthermore, the obtained precipitations were cleaned by centrifugation. After that the obtained powders were dried in an oven at 60^0C for 24 h. The obtained powders include MnS and 10%wt MWCNT doped MnS were characterized using X-ray diffraction (XRD), scanning electron microscoby (SEM) and Energy-dispersive X-ray spectroscopy (EDS). Electrochemical properties of the prepared MnS and 10%wt MWCNT doped MnS coated nickel foams were investigated using three-electrodes potentiostat/galvanostat system.

III. Results

A. *X-ray diffraction analysis*

By examining the XRD spectra of MnS and MWCNT doped carbon nanotube materials, we can learn more about the crystal structures, crystal sizes and crystal orientations of these materials. The XRD spectrum can also give clues about the purity of the material, the phase composition, and changes in the crystal structure. The fundamental peaks of 32.44, 36.34, 38.24, and 60.15^o observed in the XRD spectrum of the MnS crystal structure indicate that it has a certain crystal order. These peaks are usually the diffraction signals of certain crystal surfaces and help determine the crystalline structural properties of the material. These main peaks are in agreement with the MnS structures in the literature [9]. When the XRD spectrum of MNWCT doped MnS nanocomposites is examined, peaks are seen at 26.23, 27.90, 29.65, 32.44, 36.34, 38.49, 45.74, 50.27 and 54.50 degrees. Of these peaks, 32.44, 36.34, and 38.49 peaks are due to the MnS structure. Of the remaining peaks, the 26.23 peak can be attributed to MWCNT.

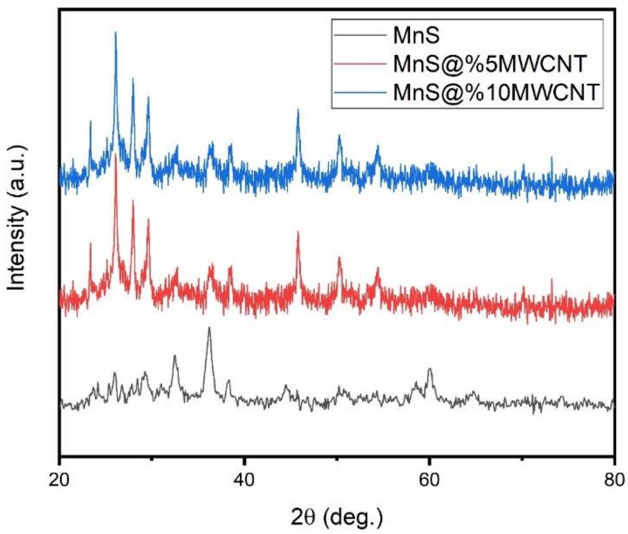

Figure 1. XRD pattern of composite of MnS, MnS@%5MWCNT and MnS@%10MWCNT

B. *Microstructure SEM and EDX analysis*

SEM images and EDX spectra of MnS and MWCNT doped MnS structures are given in Figure 2. When we examine the SEM images, it is seen that the MnS structure has a spherical morphology (Fig. 2a). When the SEM images of the materials with MnS@MWCNT structure are examined, it is seen from the SEM images that this distribution increases as the mass of MWCNT ratio increases in the structure (Fig. 2b-2c). In the EDX spectrum of the MnS structure, only Mn and S are seen in the structure (Fig. 2d). When the EDX spectra of MnS@MNWCT structures are examined, the presence of Mn, S and C is seen in the structure. In addition, as the MWCNT ratio increases, the atomic ratio of C released in EDX also increases (Fig. 2e-2f). This result confirms that the MWCNT ratio in the structure increased.

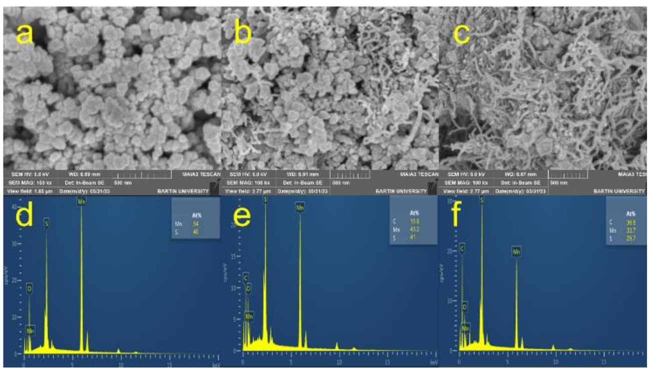

Figure 2. a)MnS, b) MnS@%5MWCNT, c) MnS@%10MWCNT SEM images, d)MnS, e) MnS@%5MWCNT, f) MnS@%10MWCNT EDX spectra

C. *Electrochemical Analyses*

In Figure 3 (a and b), the cyclic voltammetry (CV) curves of bare MnS and the MnS@MWCNT electrodes are shown for different scan rates ranging from 10 to 100 mV s^{-1} in the voltage range of -0.3 to 0.4 V. The presence of two redox peaks in the CV plots indicates the occurrence of reversible Faradaic reactions within the materials of the electrodes. Comparing the CV curves of bare MnS and the MnS@MWCNT, the latter one represented the larger area. Figure 3 (c and d) shows the galvanostatic charge-discharge (GCD) plots of pure MnS and the MnS@MWCNT at different current densities ranging from 1 to 5 A g^{-1}. The specific capacitance of the MnS@MWCNT electrode is higher compared to the bare MnS electrode which is consistent with the findings from CV measurements. Although the pure MnS electrode exhibited a high of 3940 F g^{-1} at 1 A g^{-1}, the MnS@MWCNT electrode's specific capacitance was slightly increased to 4747 F g^{-1} at the same current density. The reason why the bare MnS has remarkably high capacitance is that the growth of the MnS electrode directly on nickel foam may result in strong mechanical adhesion and efficient charge transfer routes. This eliminates the requirement for polymer binders or conducting carbon additives and significantly increase the presence of used material within the electrode matrix. Adding MWCNT to the electrode also played a crucial role in facilitating electron transfer and providing a stable structure, resulted in improved capacitance due to the enhanced electrical conductivity, excellent chemical stability, and electrical properties of MWCNTs.

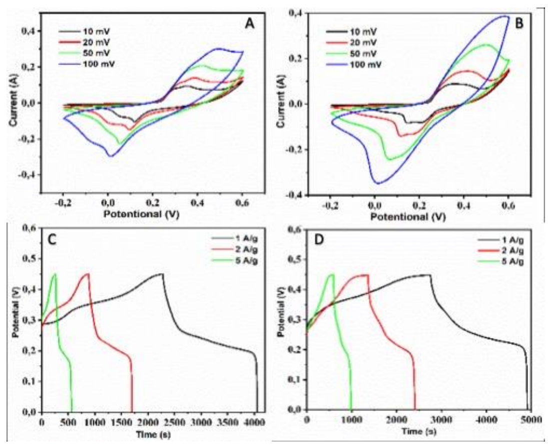

Figure 3. CV curves of a) MnS b) MnS@MWCNT, GCD plot of c) MnS d) MnS@MWCNT.

IV. DISCUSSION

In this study, the use of manganese sulfide (MnS) and multi-walled carbon nanotube (MWCNT) doped MnS nanoparticles as high capacitance supercapacitors was investigated. MnS is a promising material for supercapacitors due to its high electrical conductivity, wide electrochemical window, and favorable energy storage properties. MWCNTs, on the other hand, can provide mechanical strength to MnS nanoparticles and improve their electrochemical performance. In this study, synthesis, and characterization of MnS and MWCNTs were carried out in detail. MWCNT additive was made to provide homogeneous distribution of MnS nanoparticles and to increase electrical conductivity. Electrochemical performance evaluation was carried out using methods such as loop voltammetry and continuous charge-discharge tests. The results showed that MnS and MWCNT doped MnS nanoparticles have high capacitance values and fast charge-discharge properties. The MWCNT additive further improved the supercapacitor performance by increasing electron communication. These results show that MnS and MWCNT-doped MnS nanoparticles are a promising material combination for high-capacity supercapacitors.

V. CONCLUSION

This study reveals the potential of using MnS and MWCNT-doped MnS nanoparticles in high-capacity supercapacitors. By adding the mechanical strength and conductivity of MWCNTs to the energy storage properties of MnS, supercapacitor performance is optimized, and efficiency is increased in energy storage systems. The results of this study are an important step in the development of supercapacitor technology. MnS and MWCNT doped MnS nanoparticles can be an effective solution in energy storage systems by offering advantages such as high capacity, fast charge-discharge properties, and long life. Future studies should focus on examining the different synthesis methods and rates of MnS and MWCNT-doped MnS nanoparticles. In addition, it is important to evaluate the performance of these materials in different application areas and to investigate their effects on cyclic stability in more detail. In this way, the use potential of MnS and MWCNT doped MnS nanoparticles in supercapacitors can be further developed and more effective solutions can be obtained in the field of energy storage.

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