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Layer by layer approach to enhance capacitance using metal sulfides for supercapacitor applications

Archana Subramanian [a], Dinah Punnoose [b], Vivekanandan Raman [a], Chandu V.V. Muralee Gopi [a], Sunkara Srinivasa Rao [c], Muhammad Adil Khan [a], Hee-Je Kim [a,*]

[a] Department of Electrical and Computer Engineering, Pusan National University, Geumjeong-Gu, Jangjeong-Dong, Busan 609-735, South Korea
[b] Department of Computer Science and Engineering, Hindustan Institute of Technology and Science, Chennai 603103, India
[c] Department of Mechatronics Engineering, Kyungsung University, Busan 46241, South Korea

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ABSTRACT

Layer-by-layer approach for NiS, CoS and PEDOT:PSS (poly(3,4-ethylenedioxythiophene) polystyrene sulfonate) is being fabricated. Metal sulfides have always been chosen for their remarkable electrochemical characteristics and wide beneficial domains, such as electrochemical energy conversion and storage. This work presents the preparation of cost-effective metal sulfides (NiS, NiS/CoS, NiS/CoS/PEDOT:PSS) developed on nickel foam sheets for supercapacitor (SC) applications. The assembled NiS/CoS/PEDOT:PSS array SC device exhibits an utmost energy density of 30.3 W h kg^{-1} and specific capacitance of 353 F g^{-1}. All wet processing methods of fabrication accompanied with superior performance characteristics make these SCs very attractive for the next generation flexible energy storage systems.

1. Introduction

The worldwide trending concept of environment friendly energy conversion and storage applications serves a great impact on the development of supercapacitor/energy storage devices. Supercapacitors are accomplished with high energy density and long term cycling stability. In general, supercapacitors are classified as electric double layer capacitors (EDLCs), Pseudo-capacitors and hybrid capacitors. Currently, the most commercial supercapacitor electrode materials are made of pure carbon electric capacitive materials. They are manifested with excellent lifetime cycle and high maximal power density, but do not possess high specific capacitance or energy density to meet the ever-growing need for peak-power provisioned electric vehicles. Compared with pure carbon-based materials, pseudocapacitive materials augments specific capacitance and energy density compared to pure-carbon based materials cause of interfacial reversible faradaic reactions to store energy. Metal sulfide electrode materials are always chosen over metal oxides. It is because of good conductivity nature of sulfides. Also, the electronegativity of sulfur is less than that of oxygen providing better electron transfer. Thirdly, oxygen can be substituted by sulfur to improve flexible nature in several applications. Various composites of nickel sulfide are used in many areas like dye-sensitized solar cells and hydrogen evolution reaction (HER). Similarly, they have also been manoeuvred as supercapacitor materials in different structural forms. It is reported that compounds of mixed transition metals have superior capacitive performance than single transition metal oxides/ sulfides. Nickel and Cobalt based supercapacitors exhibit good specific capacitance and energy densities at low current densities [1]. In this work, Layer-by-Layer (LbL) dip coating has been accomplished, as it is a simple and inexpensive thin film fabrication method. The coupling of two metal species could furnish the composite transition metal oxides/sulfides with rich redox reactions and enhance the electronic conductivity, which is beneficial to electrochemical applications. Generally, nickel foam acts as a base pattern for the growth/electrodeposition of materials because of its high conductivity with porous nature. Recently, numerous transition oxide/sulfides materials has been developed on nickel foam due to its porous-form structure, which in turn confirms a huge amount of operating areas for ion diffusion and redox reaction. The focus on exploration of an ideal electrode material that matches better optoelectronic properties and good electrochemical energy storage behaviours is to be considered. This paves the way for developing a novel class of multifunctional electrode material for flexible and transparent energy conversion and storage devices. To obtain this, PEDOT: PSS has been applied over the above coated metal

* Corresponding author.
E-mail address: heeje@pusan.ac.kr (H.-J. Kim).

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sulphides [2]. In this work, metal sulfides such as Nickel Sulfide (NiS) and Cobalt Sulfide (CoS) have been coated on nickel foam hierarchically. Over which, PEDOT:PSS can be uniformly distributed to enhance the electrochemical properties of the composite metal sulfides. Herein, the supercapacitive properties of NiS/CoS/PEDOT:PSS on nickel foam will be reported.

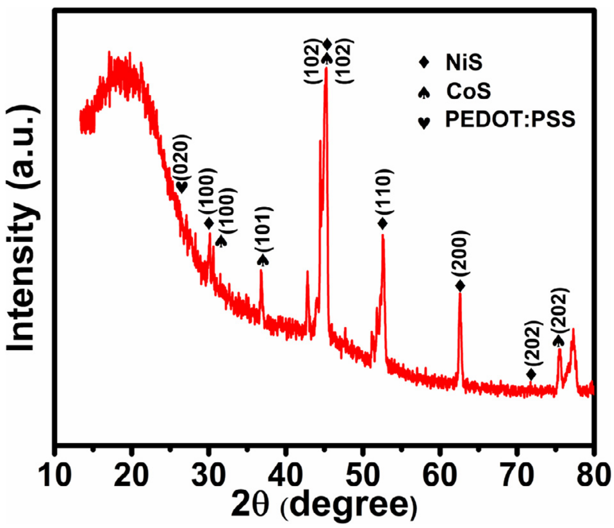

Fig. 1. XRD pattern of NiS/CoS/PEDOT:PSS substrate.

2. Experiment

2.1. Preparation of nickel foam substrate

Initially, nickel foam sheet was cut into 1 cm × 1 cm size and cleaned carefully in an ultrasonic bath sonication for 10 min using concentrated HCl solution to take off surface oxide. It was then treated with deionized (DI) water, ethanol, and acetone for 10 min each to assure the nickel foam became super clean. Later, it was kept in oven at 60 °C for 5 h.

2.2. Synthesis of NiS/CoS/PEDOT:PSS on nickel foam

All chemicals were of analytical grade and used without further purification. The host precursor materials such as 0.1 M $NiSO4 \cdot 6H2O$ and 0.05 M C3H7NO2S were stirred in DI water for 15 min. Then 1 M C2H5NS is added to the above mixture and stirred for another 15 min until it becomes homogeneous solution. Later, nickel foam was immersed in the solution and dried in oven at 80 °C for 2 h. The obtained NiS layered nickel foams were taken and cleaned thrice with DI water and ethanol, and then dried at 60 °C for 5 h.

The sources of cobalt and sulfide were taken correspondingly as 0.1 M $CoCl2 \cdot 6H2O$ and 0.1 M C2H5NS to prepare CoS solution. They were dissolved in DI water and 0.99 ml of triethanalomine. In the above solution, the NiS coated nickel foam was immersed and dried in oven at 90 °C for 1 h. Then, NiS/CoS fabricated nickel foam was taken and cleaned with DI water, and ethanol, and then dried

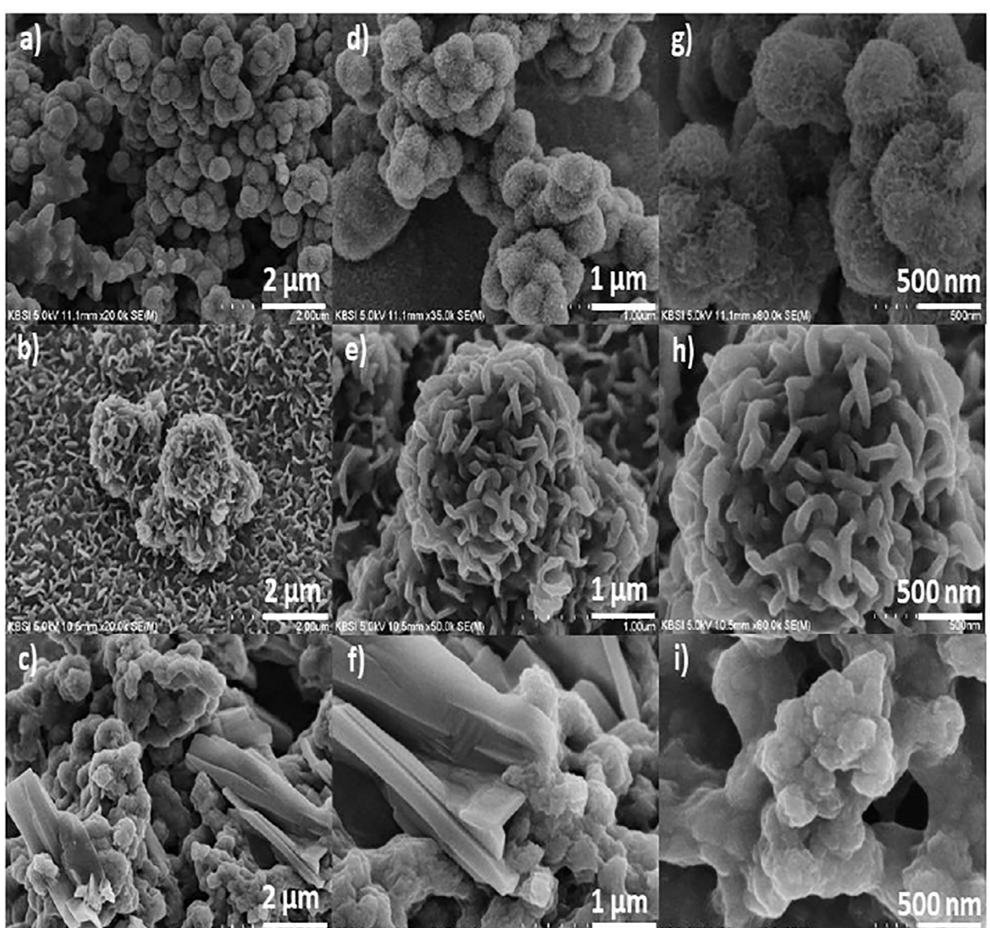

Fig. 2. FE-SEM images of NiS (a,d,g), NiS/CoS (b,e,h), NiS/CoS/PEDOT:PSS (c,f,i) substrate in the size order of 2 µm, 1 µm, and 500 nm.