One-step synthesis of binder-free Copper molybdenum sulfide for high-performance symmetric supercapacitor

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1. Introduction

Supercapacitors have considered as a vital energy storage device for the sustainable development of current and future societies and developing the industrial application. It is well known that classic supercapacitors comprise of electric double-layer capacitors (EDLCs) arising from ion adsorption/desorption, and pseudocapacitors originating from fast Faradic reactions. Recent advances in electrode materials focused on the use of 2D materials beyond graphene such as transition metal chalcogenides (MoS_2, $MoSe_2$, TiS_2, VS_2), layered MXenes (Ti_3C_2, Ti_2C), and layered transition metal oxides/hydroxides. The literature on the electrochemical properties of these layered materials suggested much efforts are needed to improve the energy density of supercapacitors using these electrodes. [1]

In this scenario, copper molybdenum sulfide (CMS) is one of the most promising LTMCs with fascinating properties such as electrochemical energy storage, photocatalysis and electrochemical hydrogen evolution. Herein, we fabricated CMS grown on Ni foam and investigated their capacitive properties using symmetric supercapacitor design.

2. Experimental section

A one-pot hydrothermal method was used for the preparation of CMS nanostructure on Ni foam. In a typical synthesis, 60 mg of $Na_2MoO_4.2H_2O$ and 120 mg of CH_3CSNH_2 was dissolved in 60 mL of ethylene glycol by ultra-sonication for one hour. Then 40 mg of Cu_2O was added slowly to the above precursor solution and kept it for ultra-sonication for two h to form a dark brown solution. After that, the precursor solution was transferred to a 100 mL Teflon lined stainless steel autoclave. The cleaned piece of Ni foam was immersed in the dark brown solution and kept at 150 °C for 15 h. After completion of the hydrothermal reaction, the autoclave was allowed to cool to room temperature naturally and collected the obtained precursor grown on Ni foam. Ni foam was cleaned by ultrasonication approach using repeated rinses of water and absolute ethanol. Finally, the collected Ni foam was dried at 60 °C for 4 h.

3. Results and discussion

The CMS nanostructures were grown directly on the surface of Ni foam via a hydrothermal reaction. The field emission-scanning electron microscope (FE-SEM) analysis of CMS grown on Ni foam is shown in Fig. 1. The FE-SEM micrographs given in Fig. 1 shows the homogeneous growth of CMS nanostructures on the surface of Ni foam with size in the range of 100 to 200 nm. The formation of CMS nanostructure can be explained as follows: During the hydrothermal reaction, the MoO_4^{2-} ions and sulfur ions (released from the sodium molybdate and thioacetamide) reacts together which results in the formation of MoS_4^{2-} ions via nanoscale Kirkendall effect. Later, the Cu_2O particles reaction with the MoS_4^{2-} ions which results in the formation of CMS anchored on Ni foam.

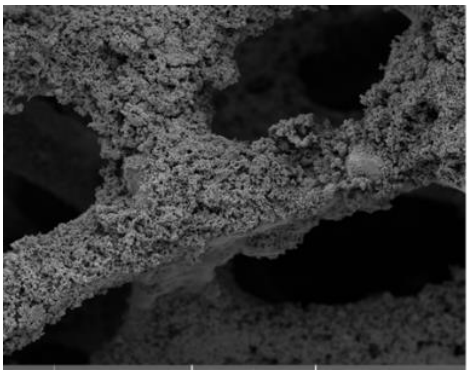

Fig. 1 FE-SEM micrographs for CMS grown on Ni foam

Figure 2 represents the XRD pattern of CMS grown on Ni foam. The diffraction peaks obtained at 2θ = 16.73°, 21.87°, 29.12°, 31.02°, 37.54°, 46.20°, 48.54°, and 55.40°, corresponding to the (002), (110), (112), (013), (004), (123), (220) and (132) crystal planes of tetragonal Cu_2MoS_4 as reported in the previous literature [2,3]. Three extra peaks (*) observed at 2θ = 44.32°, 51.69° and 76.14° correspond to the Ni foam (current collector).

The as-prepared CMS anchored on Ni foam is examined as an electrode material for supercapacitor by fabricating symmetric

supercapacitor cell (SSC) using 1 M Na_2SO_4 solution as an electrolyte.

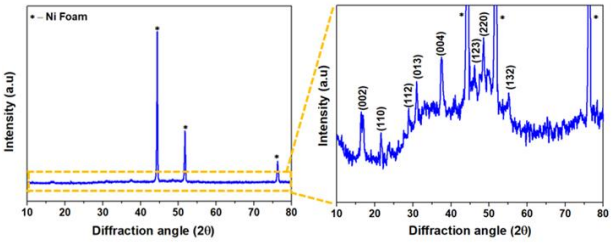

Fig. 2 XRD pattern of CMS grown on Ni foam, peaks denoted to (*) correspond to Ni foam.

The CV profiles of the CMS/Ni SSC obtained using different scan rates is shown in Fig. 3, which displayed a typical rectangular behavior, thus indicating the ideal capacitive properties of the CMS/Ni SSC [4,5]. The CMS SSC device possesses a high specific capacitance of about 219.91 F g^{-1} obtained from the CV profiles recorded at 5 mV s^{-1}.

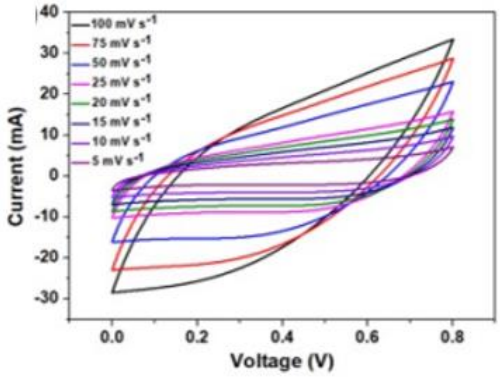

Fig. 3 Cyclic voltammetric (CV) profiles of CMS/Ni SSC at different scan rate

The CD profiles of CMS/Ni SSC recorded using different current of 5 to 25 mA is presented in Fig. 4. The CD profiles revealed the presence of sloppy-symmetric triangular shaped nature as evidence of pseudocapacitive nature of CMS/Ni SSC. The CMS SSC device possesses a high specific capacitance of about 265.62 F g^{-1} obtained from the CD profiles recorded at 5 mA.

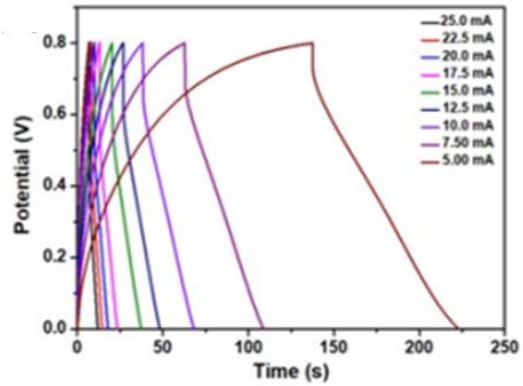

Fig. 4 Charge-discharge (CD) profiles of CMS/Ni SSC measured at different current.

The CMS/Ni SSC possesses a high energy density of 23.61 Wh kg^{-1} with a corresponding power density of 1000 W kg^{-1} obtained from the CD profile recorded using a current of 5 mA. With a five-fold increase in current, the CMS/Ni SSC still holds an energy density of 6.80 Wh kg^{-1} whereas the power density increases up to 5000 W kg^{-1}, respectively.

4. Conclusions

The electrochemical analysis of the CMS/Ni SSC revealed the superior charge storage performance with a high specific capacitance (265.62 F g^{-1}), high energy density (23.61 Wh kg^{-1}), and excellent cyclic stability. Collectively, this study demonstrated the potential use of binder-free CMS/Ni electrode as a high-performance electrode towards the development of next-generation supercapacitors.

Acknowledgment

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