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One step sputtered grown MoS_2 nanoworms binder free electrodes for high performance supercapacitor application

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ABSTRACT

Two-dimensional (2D) materials have attracted significant attention for device applications due to their unique structural, electronic and catalytic properties. In this manuscript, worms like nanostructures of MoS_2 were directly deposited in the form of thin films on a copper substrate using DC magnetron sputtering technique and further it is utilized as supercapacitor electrode without additional processing. The binder free MoS_2 nanoworms symmetric supercapacitor device delivered a high capacitance (138 F/g at 1 A/g), excellent cycling ability (86% over 5000 cycles), along with high energy density (ED) and power density (PD). These observed excellent electrochemical performances of the present MoS_2 nanoworms based electrodes, suggest its tremendous potential as supercapacitor electrodes in energy storage applications.

Introduction

Supercapacitors are very promising energy storage devices because of their rapid charging/discharging time, high power density and long cycle life than that of conventional batteries and regular capacitors [1–3]. Supercapacitors can be divided into two groups on the basis of charge storage mechanism; (1) Electric Double Layer Capacitors (EDLCs) and (2) Pseudocapacitors [4,5]. In EDLCs, energy storage takes place due to the accumulation of ions between the electrode and the electrolyte. On the other hand Pseudocapacitors use the reversible redox reactions between the electrode and the electrolyte to store the charges [6]. EDLCs have long cyclability with small degradation but have lower specific capacitances as compared to Pseudocapacitors [7]. Currently employed supercapacitors have lower energy density than that of rechargeable batteries, so extensive efforts have been made on increasing the energy density of supercapacitors. The performance and the quality of supercapacitors highly depend on fabrication methods and advanced electrode materials [8,9]. In

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most of the fabrication methods, the occurrence of an inactive surface due to the use of conductive agents and polymer binders in the normal slurry coating process, hinders the accessibility of electrolyte ions [10,11]. Therefore, the development of low-cost, simple and polymer binder free supercapacitor electrodes can improve the storage properties [12–15]. Physical vapor deposition (PVD) techniques, mainly thermal evaporation and sputtering have been considered as an eloquent way to synthesize high-quality contamination free nanostructures for supercapacitor electrodes [16].

Intrinsic two-dimensional (2D) materials and nanostructure are very promising candidates for supercapacitors due to high surface area and enhanced capability of charge storage [17]. One group of 2D materials is the transition metal dichalcogenides (TMDs). TMDs are interesting candidates for different applications such as photovoltaic devices, energy storage devices, valleytronics, low power logic devices, spintronic etc [18–26]. Nanostructures of 2D TMDs have unique electrical, optical, thermal and mechanical properties [27–31]. Chemical formula of TMDs is MX_2, where M is the transition metal atom (e.g. Mo, W, Nb, Ta, Ti, Re etc.) and X is chalcogen atom (e.g. S, Se & Te) [32]. TMDs are an interesting family of 2D materials which have layered structure (X-M-X) and consist of a hexagonally packed transition metal atom layer sandwiched between two chalcogen atom layers [22,28,29].

Molybdenum disulphide (MoS_2) is the most extensively studied TMD, because of its excellent optoelectronic, nanoelectronic and energy harvesting properties [33]. Recently, MoS_2 nanosheets based supercapacitors have attracted great attention due to their nanosheets like structure, which provides large surface area for double layer charge storage [34–36]. MoS_2 has a layered structure with strong *in-plane* covalent bonds and separated by weak Van der Waals bonding [37–40]. The excellent intrinsic property of this 2D material is its tunable energy band gap. The band structure of MoS_2 changes from indirect to direct bandgap on reducing the number of layers from few layers to monolayer which results in a unique sensitivity of MoS_2 properties to thickness [41,42].

MoS_2 thin films can be synthesize by various techniques such as mechanical exfoliation, Sputtering, hydrothermal synthesis, chemical vapor deposition (CVD) etc [43,44]. Here, high quality MoS_2 thin films having nanoworms like structures for supercapacitor electrodes were deposited using DC sputtering technique. Sputtering technique provides uniform and large-scale deposition of thin films with better adhesion without any polymer binder. The electrochemical characteristics of the directly fabricated MoS_2 nanoworm thin film supercapacitor electrodes have been investigated on the basis of cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) cycles, and electrochemical impedance spectroscopy (EIS), and the results are discussed in detail.

Experimental

Materials and chemicals

MoS_2 target (2″ diameter) of high purity (99.99%) were purchased from Testbourne Ltd. UK. Copper (Cu) foil substrate were purchased from Sigma Aldrich (1 mm thickness, 99.98% pure trace metal basis). Argon (Ar) gas cylinder of high purity (99.9%) was purchased from Sigma Gases, India. Sodium sulphate (Na_2SO_4) were obtained from Merck, India. Deionized water was used for electrochemical anodization.

Preparation of working electrode

MoS_2 nanoworm like thin films were grown on Cu foil (1 cm^2, and sequentially cleaned in acetone, isopropyl alcohol, and deionized water and dried in nitrogen atmosphere) by DC sputtering technique. Initially, the chamber was evacuated to 5×10^{-6} Torr using turbo molecular pump. After the evacuation of the chamber, a negative bias is applied to target material and Argon (Ar) gas was introduced into the sputtering chamber which serves as the discharge medium. The working pressure in the chamber was kept at 5 mTorr. The distance between target material and substrate holder was kept at 6 cm MoS_2 films of different thicknesses were deposited on Cu substrate by applying 45 W power at 300 °C for a period of 30 min. The loading mass of active material MoS_2 on Cu current collector was about 1.2 mg. The symmetric supercapacitor device was assembled by using two MoS_2 working electrodes with a separator (Whatman, Grade GF/C) and 1 M $Na2SO_4$ aqueous electrolyte.

Structural characterization

The surface morphologies and structural characterizations of fabricated samples were characterized by field emission scanning electron microscopy (FE-SEM, Carl Zeiss Ultra plus), energy dispersive X-ray analysis (EDAX, Oxford Instruments), atomic force microscopy (AFM, NT MDT-NTEGRA), X-ray diffractometer (XRD, Bruker AXS, D8 advance), Transmission electron microscope (FEI, Quanta), and Raman spectrophotometer (Renishaw, United Kingdom). Electronic nature of the films was studied using X-ray photoelectron spectroscopy (XPS, PHI Versa Probe III electron spectrometer).

Electrochemical characterization

CV curves were measured using an electrochemical workstation (CHI 660D) to evaluate the specific capacitance (C_s) using a well-known equation

$$C_s = \frac{\int I(V)dv}{\nu m \Delta V} \quad (1)$$

where, $\int I(V)dv$ is the integral area of the CV curve (AV), ν is the scan rate (mV/s), m is the mass of the active material (g), and ΔV is the potential window (V) [45]. The details of the active material calculation are described in the authors' previous study [46].

GCD cycles were measured within a voltage range of 0–0.8 V at different current densities to evaluate the specific capacitance (C_s) using a familiar equation

$$C_s = \frac{i \times \Delta t}{m \times \Delta V} \quad (2)$$

where i is the discharge current (A), Δt is the discharge time (s), m is the mass of the active material (g) and ΔV is the discharge potential with subtracting potential (IR) drop [47].

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