Controlled synthesis of nanostructured molybdenum oxide electrodes for high performance supercapacitor devices

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ARTICLE INFO

ABSTRACT

Well defined crystallographic and one dimensional morphological structure of molybdenum oxide were successfully synthesized by adjusting the duration of hydrothermal treatment. The prepared molybdenum oxide was examined through XRD, SEM, FTIR, TEM, BET and electrochemical studies. The XRD patterns illustrate that MoO_x prepared by variying the hydrothermal reaction time are in different crystallographic structure of Mo_yO_x (Mo_8O_{23} and MoO_3). SEM studies reveal the different morphological structures ranging from flake like morphology to nanorods. TEM images confirm the excellent nanorod structure. The nanorod structure ensures good cyclic behaviour with maximum capacitance of $1080 \, F \, g^{-1}$ at a current density of $2 \, A \, g^{-1}$. This large capacity of the MoO_3 nanostructures enabled fabrication of symmetric and asymmertic supercapacitor devices. The asymmertic device exhibits a maximum specific capacitance of $145 \, F \, g^{-1}$ at $2 \, mV \, s^{-1}$ with highest energy density of $38.6 \, W \, h \, kg^{-1}$ at $374.7 \, W \, kg^{-1}$ power density.

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1. Introduction

On account of the energy crisis and dwindling reserves of fossil fuels, mankind is forced to look for renewable and sustainable energy resources. Some of these need energy stroage devices for useful exploitation. Appropriate and efficient energy stroage systems are required to store electricity generated from renewable resources. Among these, the electrochemical energy stroage devices are more viable and environmental friendly. Due to high energy density, excellent cyclic performance and ultra fast charge–discharge rates, supercapacitors provide great impetus in the field of electrochemical energy stroage systems [1,2]. Several efforts have been devoted to develop nanostructured materials for high performance solid state supercapacitors. Due to the fast redox reaction and various crystallographic structures, the nanostructured metal oxides have become important for electrochemical energy stroage devices [3]. Transistion metal oxides/hydroxides, such as MnO_2 [4], $Co(OH)_2$ [5], V_2O_5 [6] have been comprehensively used as supercapacitor electrodes for the enhanced specific capacitance and power density. Among them, molybdenum oxide (MoO_3) is endowed with the following significant properties: ample resources in nature, more valance states with outstanding theoritical specific capacitance ($2700 \, F \, g^{-1}$), high electrochemical activity for supercapacitors. MoO_3 is a distinguished transition

metal oxide with structural litheness, rich polymorphism and very stable layered structure (two-dimensional (2D)) [7]. The bilayered structure of MoO_6 octahedra is knowned to be formed by van der waal forces [8–10]. These structures are beneficial for the permeation of small ions such as H^+, Na^+ and K^+. However, its low electronic conductivity and lack of structural reliability during electrochemical reactions are adverse to long-term cyclic performance in electrochemical devices [11,12]. Many efforts have been made to improve the cyclic stability and specific capacitance of the MoO_3 supercapacitor [13,14]. Several experimental and computational studies have proved that the electrochemical performance is largely influenced by the crystal structure and morphology of the electrode material [15–20]. Therefore, size and shape controlled nanomaterials are essential to understand and evaluate their intrinsic properties [21–24]. In the present work, we report a simple hydrothermal method for the synthesis of molybdenum oxide (Nanoflakes, Microrods and Nanorods) with SDS as the capping agent under different hydrothermal durations. The prepared materials were investigated as supercapacitor electrode material in an aqueous electrolyte. It is found that molybdenum oxide with desired structure delivers improvement in their high specific capacitance and cyclic stability. Li-Jun Bian et al. [25] reported polyaniline doped MoO_3 nanorods to exhibit a specific capacitance of $570 \, F \, g^{-1}$ at $1.7 \, A \, g^{-1}$ while a symmetric device fabricated by them could provide the specific capacitance ($130 \, F \, g^{-1}$ at $1.3 \, A \, g^{-1}$) and an energy density of $35 \, W \, h \, kg^{-1}$ at a power density of $4.7 \, kW \, kg^{-1}$. Maximum capacitance of $250 \, F \, g^{-1}$ at a current density of $0.25 \, A \, g^{-1}$ could be obtained by Kumar et al. [3] with h-MoO_3 nanorods. In the cur-

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rent investigation, we report a simple shape controlled synthesis of pristine molybdenum oxide material (without any self dopant or addition agent) employed as electrodes for asymmetric and symmetric solid state supercapacitor with a gel electrolyte. Here we have altered the duration of hydrothermal treatment to modify the morphology and structure of the particles obtained. An asymmetric supercapacitor based on the nanorod structured molybdenum oxide exhibits excellent energy density of 38. 62 W h kg^{-1} with a power density of 374.8 W kg^{-1}. Compare with the literature, it can be notice that only few reports on the supercapacitor behaviour of pristine molybdenum oxide [3,4,26]. To the best of our knowledge, this the finest supercapacitor performance, in particular with specific capacitance, cyclic stability and energy density value, compared to those reported in the literature [4,26].

2. Experimental details

2.1. Synthesis of molybdenum oxide material

Chemical reagents used for the present synthesis processes are of analytical grade and have been used as received without further purification. Hydrothermal method was employed to synthesis molybdenum oxide nanostructures. Typically, 2.3278 g of ammonium heptamolybdate tetrahydrate $(NH_4)_6Mo_7O_{24}\cdot4H_2O)$ was dissolved in 20 mL of H_2O_2. 0.05 M of SDS (sodium dodecyl sulphate) was dissolved in 20 mL of water and was added to the ammonium heptamolybdate tetrahydrate solution. This mixture was stirred continuously for 30 min using a magnetic stirrer. The pH of the solution was adjusted to 3 with the addition of dilute HCl drop wise under constant stirring. Thus obtained transparent solution was subjected to hydrothermal treatment using Teflon-lined stainless steel autoclave and kept at 180 °C for 4 h, 8 h, 12 h respectively. Finally, the solution was allowed to cool to room temperature. The precipitate formed following this process was washed with deionized water and ethanol several times. The final product was dried at 80 °C for 24 h. The prepared samples were calcined at 400 °C for 3 h. The products these obtained products were labelled as Mo-4, Mo-8 and Mo-12. For example, the sample synthesized through hydrothermal treatment for 4 h is termed as Mo-4.

2.2. Characterization techniques

The prepared molybdenum oxide properties were investigated using X-ray diffraction, scanning electron microscopy, FTIR spectrometry, cyclic voltammetry, chronopotentiometry and electrochemical impedance spectroscopy. X-ray diffraction patterns of samples were found using XPERT-PRO PANalytical diffractometer with CuKα (λ = 1.54060 Å) radiation. The FTIR spectra were measured using Perkin-Elmer Spectrum BX-II spectrometer. Morphology of the samples was studied through TESCAN VEGA-3 LMU instrument. The specific surface area of the sample was obtained by the Brunauer–Emmett–Teller method using Micrometeritics ASAP 2020 analyzer. The pore size distribution of the material was generated from desorption isotherm using Barrett–Joyner–Halenda (BJH) method.

2.3. Electrode preparation and their electrochemical behaviour

Electrochemical analysis of the prepared molybdenum oxide materials was performed in the three electrode configuration with the help of CHI660D electrochemical workstation. A platinum wire was used as the counter electrode, SCE acted as the reference electrode and the prepared molybdenum oxide material (active material) served as the working electrode. 1 M H_2SO_4 aqueous electrolyte was employed as the electrolyte. The electrode was prepared by mixing (80:15:5) of active material, activated carbon and PTFE (binder) along with few drops of ethanol as the solvent. 1 mg
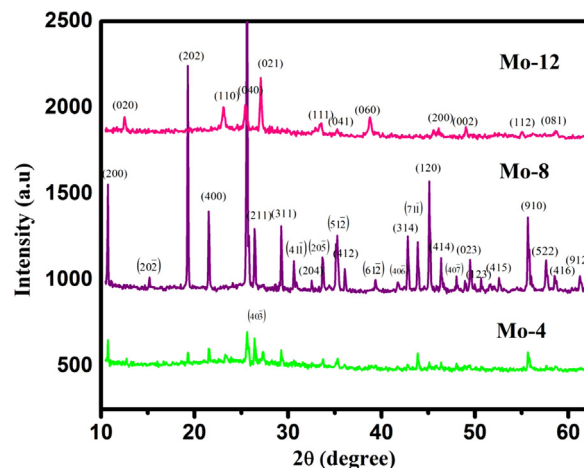

Fig. 1. XRD pattrens of molybdenum oxide.

of active material was coated on a pretreated (1 cm × 1 cm) graphite sheet substrate. The prepared electrode was dried at 70 °C for 12 h. The cyclicvoltammetry measurements of the MoO_3 electrodes were performed at various scan rates in a potential window of 0–0.8 V. The charge–discharge characterization was carried at different current densities in a potential window of 0 to 0.8 V. Electrochemical impedance measurements were carried out between 0.01 Hz and 100 kHz with AC amplitude of 5 mV and bias potential of 0.35 V.

2.4. Assembly of solid state symmetric and asymmetric supercapacitors

The asymmetric solid state supercapacitors (MoO_3//AC) were assembled using the MoO_3 nanorod arrays as a positive electrode and activated carbon as the negative electrode. PVA–H_2SO_4 gel electrolyte was prepared by mixing 1 g H_2SO_4 and 1 g PVA in 10 mL of distilled water. It was heated to 80 °C under vigorous stirring until the solution became transparent. Prior to assembly, the two electrodes (each has mass loading 1 mg) were soaked in the PVA–H_2SO_4 solution for 5 min. Then the gel was allowed to solidify at ambient temperature for 12 h. Finally, two electrodes were assembled carefully to get the asymmetric solid state supercapacitor. In the case of symmetric supercapacitor, both positive and negative electrodes are made up of MoO_3 (MoO_3//MoO_3).

3. Results and discussions

3.1. Structural and Morphological analysis

The crystallographic structures of the prepared materials were estimated by x-ray diffraction measurements. XRD pattern of the molybdenum oxide nanoparticles is presented in Fig. 1. Mo-4 and Mo-8 particles show diffraction peaks corresponding to (200), (201), (202), (40$\bar{1}$), (400), (010), (40$\bar{2}$), ($\bar{2}$00), (405), (11$\bar{2}$) and (203) planes of the monoclinic Mo_8O_{23}. This agrees well with the JCPDS card (74-1661). In case of Mo-12, the peaks are indexed to the orthorhombic structured MoO_3, which is consistent with the standard values of bulk MoO_3 (JCPDS card no: 89-5108) with space group pbnm (62) and lattice parameters a = 3.962, b = 13.85, c = 3.701. Yan Xu et al. [27] reported proper combination of acidity, hydrothermal condition and units of structure direction to lead to the formation of diverse geometrical and structural characteristics of molybdenum oxide. In the present study, a change in the hydrothermal duration may be the major reason for obtained different crystal structures of molybdenum oxide particles as every other condition was maintained constant.