One-dimensional MoO$_2$ nanorods for supercapacitor applications

Janarthanan Rajeswari, Pilli Satyananda Kishore, Balasubramanian Viswanathan [*],
Thirukkallam Kanthadai Varadarajan

National Centre for Catalysis Research, Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India

ABSTRACT

One-dimensional (1D) MoO$_2$ nanorods were prepared by thermal decomposition of tetrabutylammonium hexamolybdate ($((C_4H_9)_4N)_2Mo_6O_{19}$) in an inert atmosphere. The synthesized nanorods have been characterized by XRD, TEM and HRTEM. The capacitive behaviour of 1D MoO$_2$ nanorods was studied by galvanostatic charge–discharge studies in 1 M H$_2$SO$_4$ solution at different current densities. The results indicate that the MoO$_2$ nanorods show good capacitive behaviour with a specific capacitance of 140 Fg^{-1}.

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1. Introduction

Electrochemical capacitors are energy storage devices that exhibit high power density, excellent pulse charge–discharge properties and long cycle life [1]. They are promising power sources for portable systems and automotive applications [2]. The most widely investigated metal oxide for pseudocapacitors is unequivocally ruthenium oxide, which displays a fairly high specific capacitance [3,4]. However, the high cost of RuO$_2$ has prompted the search for other transition metal oxides such as MnO$_2$, NiO$_x$, MoO$_3$, Co$_3$O$_4$, Fe$_3$O$_4$ and V$_2$O$_5$ [5–8]. Recent reviews have shown that the next progressive step to achieve high specific capacitances will be to design nanostructures of pseudocapacitive materials such as oxides, nitrides and carbides [9,10]. By doing so, the electrode/electrolyte contact area can be increased as charge is stored in the first few nanometers from the surface. Consequently, it is possible to maximize the contribution of the active material to capacitance. Further, nanostructured electrodes provide improved power delivery and increased cycling stability. Among the various nanomaterials, the 1D nanostructures such as nanorods, nanotubes and nanowires possess great potential of addressing space-confined transport phenomena as well as applications [11]. In particular, one-dimensional nanomaterials of metal oxides were proved to be efficient in electrochemical capacitors, batteries and fuel cells [12–14].

Herein we have employed 1D MoO$_2$ nanorods as electrodes for electrochemical capacitors. Molybdenum oxides (MoO$_2$ and MoO$_3$) have significant uses in energy related devices such as fuel cells

and lithium batteries [15–17]. Reports are available on the application of poly(3,4-ethylenedioxythiophene)–MoO$_3$ nanocomposites, MoO$_3$ nanowires, MoO$_3$ supported on activated carbon or glassy carbon materials as electrodes for supercapacitors [18–22]. However, the application of MoO$_2$ nanorods as supercapacitor electrode materials is not yet studied. Due to their low cost and good electronic conductivity, MoO$_2$ can also constitute a good electrode material for supercapacitors. There are several methods for the preparation of 1D nanomaterials of molybdenum oxides such as electrodeposition, thermal evaporation, hydrothermal, template assisted and direct oxidation of molybdenum [23–31]. Recently, we have developed a method for the synthesis of WO$_3$ nanorods by the thermal decomposition of tetrabutylammonium decatungstate. The synthesized nanorods were proved efficient for electrochemical methanol oxidation and hydrogen evolution reactions [32,33]. This has inspired us to follow the same strategy for the synthesis of molybdenum oxide nanorods and their application towards electrochemical energy storage. In this paper, we report the synthesis of 1D MoO$_2$ nanorods by thermal decomposition of tetrabutylammonium hexamolybdate ($((C_4H_9)_4N)_2Mo_6O_{19}$). The electrochemical performance of MoO$_2$ nanorods for supercapacitors was investigated by galvanostatic charge–discharge method.

2. Experimental

2.1. Synthesis of MoO$_2$ nanorods

Tetrabutylammonium hexamolybdate ($((C_4H_9)_4N)_2Mo_6O_{19}$), the precursor compound for the preparation of MoO$_2$ nanorods was prepared according to the method described by Che et al. [34]. In

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* Corresponding author. Tel.: +91 44 2257 4241; fax: +91 44 2257 4202.
E-mail address: bvnathan@iitm.ac.in (B. Viswanathan).

a typical procedure, acetic anhydride was added to sodium molybdate stirred in dimethyl formamide, followed by acidification with concentrated hydrochloric acid. The hot solution was filtered and the yellow filtrate was precipitated with a solution of tetrabutylammonium bromide in dimethylformamide. The salt obtained was filtered, washed with ethanol and ether, and finally recrystallized from acetone. The resultant precursor was taken in a quartz boat and introduced inside a tubular furnace and heated at

600 °C at a heating rate of 25 °C/min under N_2 atmosphere for 3 h. This was followed by gradual cooling to room temperature to obtain the MoO_2 nanorods.

2.2. Characterization of MoO_2 nanorods

X-ray diffraction (XRD) patterns were obtained by a powder diffractometer (SHIMADZU XD-D1) using a Ni-filtered CuKα X-ray radiation source. Transmission electron microscopy (TEM) and energy dispersive X-ray analysis (EDAX) were performed on a Philips CM12/STEM instrument. High-resolution transmission electron microscopy (HRTEM) was carried out on a JEOL 3010.

2.3. Electrochemical measurement and electrode preparation

A three electrode cell consisting of the glassy carbon as working electrode (0.07 cm^2), Pt wire and Ag/AgCl (satd. KCl) electrodes as counter and reference electrodes, respectively, were used. Galvanostatic charge–discharge studies were performed using a CHI660A potentiostat/galvanostat. The working electrodes for electrochemical measurements were fabricated by dispersing 5 mg of the catalyst in 100 μl of deionized water by ultrasonication for 20 min. From this dispersion 10 μl has been taken and placed on a glassy carbon electrode. The solvent was slowly evaporated by placing the electrode in an oven at 70 °C. Nafion solution (5 μl) has been coated on the electrode as a binder and dried at room temperature. H_2SO_4 (1.0 M) was used as the electrolyte. The electrolyte solution was deaerated with high purity N_2 (99.99%) for 30 min before the electrochemical measurements.
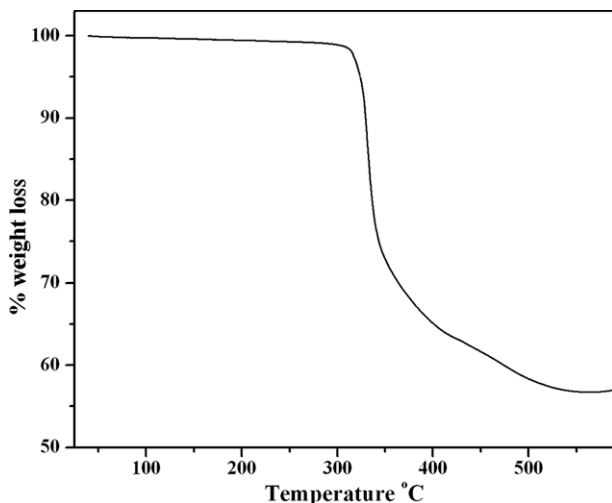

Fig. 1. Thermogravimetric analysis (TGA) of $((C_4H_9)_4N)_2Mo_6O_{19}$ in N_2 atmosphere.
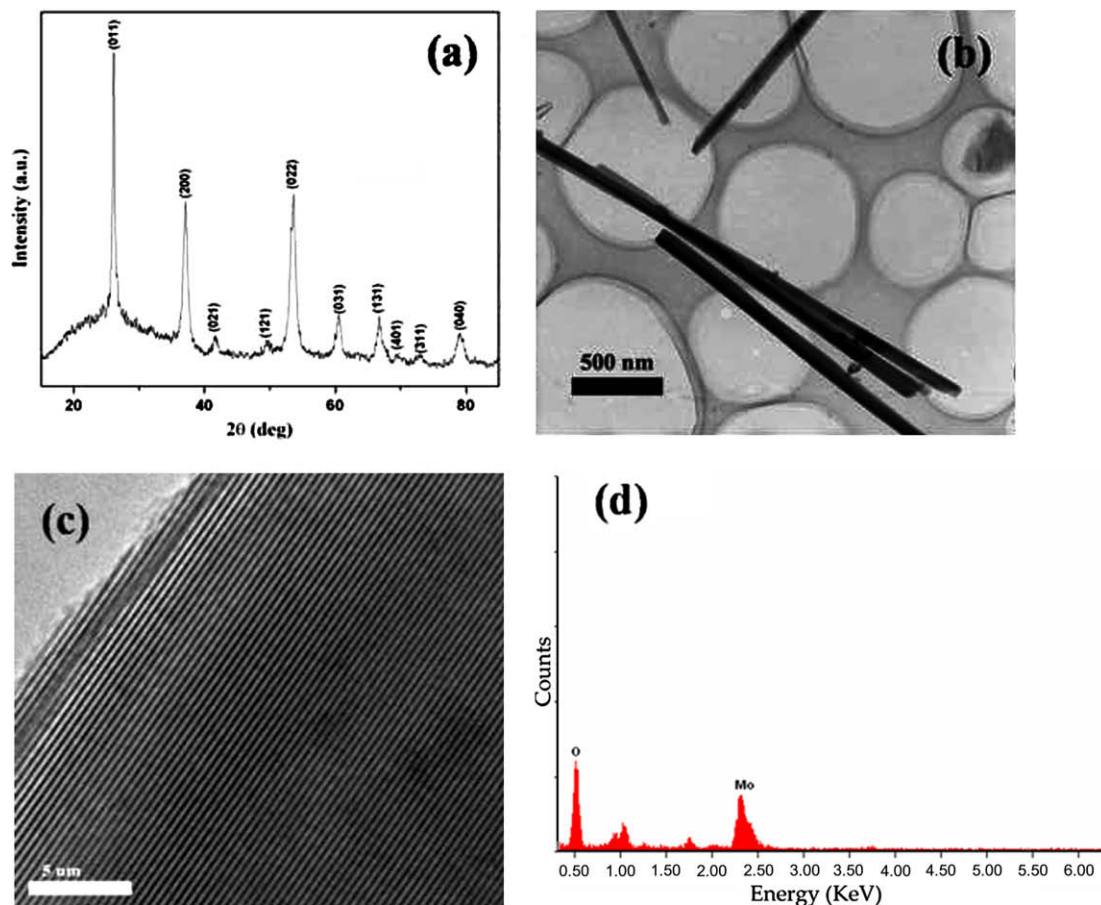

Fig. 2. (a) X-ray diffraction pattern (XRD), (b) TEM, (c) HRTEM and (d) EDAX of as synthesized MoO_2 nanorods.

3. Results and discussion

Thermogravimetric analysis of $((C_4H_9)_4N)_2Mo_6O_{19}$ from 0 to 600 °C under N_2 atmosphere is shown in Fig. 1. An initial loss of 35% (observed from TGA, Fig. 1) from 300 to 410 °C correspond to the removal of two tetrabutylammonium $[Bu_4N]^+$ groups (theoretically, 35.5%). An additional loss of about 7.5% was observed between 410 and 550 °C due to the decomposition of the $Mo_6O_{19}^{2-}$. The remaining mass, 57.5% corresponds to $6MoO_2$ (theoretically, 56.2%).

X-ray diffraction measurements confirmed that molybdenum oxide (MoO_2) are obtained by the thermal decomposition of $((C_4H_9)_4N)_2Mo_6O_{19}$ at 600 °C under N_2 atmosphere. As shown in Fig. 2a, all diffraction peaks were indexed undisputedly to monoclinic MoO_2 as confirmed from the reported data [JCPDS no. 76-1807]. The TEM image of the as synthesized MoO_2 (Fig. 2b) shows nanorods having dimensions varying in the ranges of 1–3 μm and 50–80 nm of length and width, respectively. Further, the HRTEM image analysis showed the lattice fringes of the as synthesized nanorods (Fig. 2c). The calculated space between the fringes was about 0.17 nm and it corresponds to the interplanar spacing of $(0\,2\,2)$ planes of monoclinic MoO_2. This observation is in agreement with the XRD result (JCPDS no. 76-1807). The EDAX (Fig. 2d) result confirmed the presence of respective constituent elements in MoO_2 nanorods. Thus the findings indicate that the as synthesized materials are nanosized one-dimensional molybdenum oxide materials.

Fig. 3 shows the galvanostatic charge–discharge curves of MoO_2 nanorods in 1.0 M H_2SO_4 electrolyte in the potential range between −0.3 and +0.4 V at different current densities. The specific capacitance has been calculated from the Eq. (1).

$$\text{Specific Capacitance}, C(F/g) = \frac{i\Delta t}{m\Delta V} \tag{1}$$

where i (mA cm^{-2}) is the current density used for charge/discharge, Δt (s) is the time elapsed for the discharge cycle, m is the weight of the active electrode and ΔV is the voltage interval of the discharge. The specific capacitances calculated from each discharge curve in Fig. 3 were 140, 115 and 30 Fg^{-1} at 1, 3 and 5 mA cm^{-2}, respectively. At low current densities, due to the low ohmic drop, the inner active sites or the pores of the electrode can be fully accessed; hence high specific capacitance values can be achieved [35]. Decrease in capacitance value with increasing current density has also been attributed to the slow rate of redox reactions [36]. The ob-
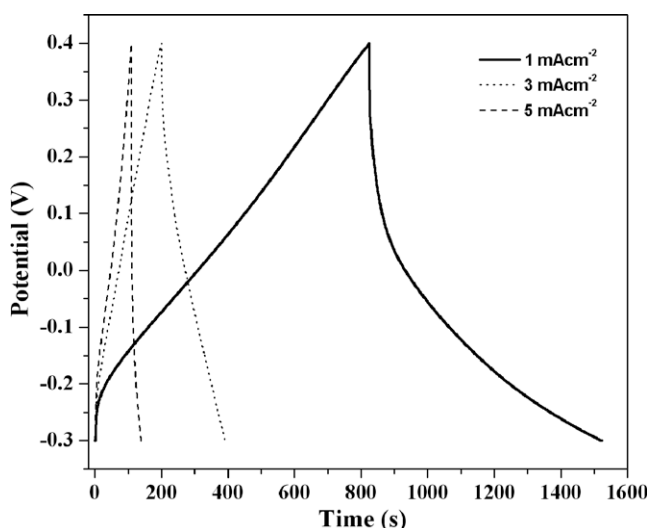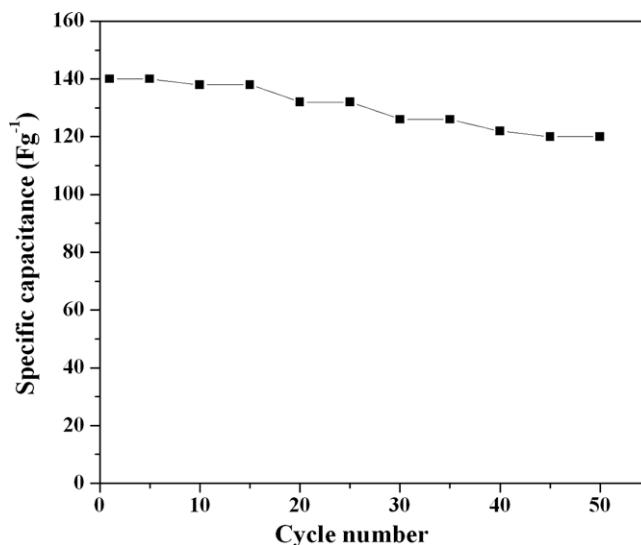

Fig. 4. Dependence of specific capacitance of MoO_2 nanorods on the number of cycles at a current density of 1 mA cm^{-2}.

served specific capacitance values for the MoO_2 nanorods are higher than the values reported for some inexpensive oxides such as NiO [5], Co_3O_4 [6] and SnO_2 [37]. In the present study, the pseudocapacitance of MoO_2 is based on the redox process that takes place in the redox transition $Mo^{4+} \rightarrow Mo^{6+}$ [15]. Asymmetric hybrid capacitors are receiving attraction as they are aimed to provide both high energy as well as power density. In an asymmetric hybrid capacitor, different materials with different operating potentials as positive and negative electrodes are employed to obtain a large electrochemical window and high specific energy density [38]. Hybrid electrochemical capacitors employ positive electrode with electroactive materials having large positive cutoff potential and negative electrode with electroactive materials having high hydrogen overpotential [39]. MoO_2 nanorods were observed to show hydrogen evolution at potentials more negative than −0.4 V vs. Ag/AgCl. Also, the redox transition $Mo^{4+} \rightarrow Mo^{6+}$ in MoO_2 occurs in the potential at around 0.2 V vs. Ag/AgCl. Hence the charge–discharge studies were performed in the potential range between −0.3 and +0.4 V vs. Ag/AgCl (satd. KCl). The electrochemical studies suggest that MoO_2 nanorods can be potential negative electrodes for asymmetric hybrid electrochemical capacitors.

The charge–discharge studies were performed at constant current density of 1 mA cm^{-2} and the variation of specific capacitance for 50 cycles is shown in Fig. 4. The electrode exhibited good reversibility with cycling efficiency of 86% after 50 cycles.

4. Conclusions

A simple and easy method based on thermal decomposition was adopted to fabricate 1-D nanorods of MoO_2. The as synthesized MoO_2 nanorods exhibited a significant value of specific capacitance which can be attributed to the unique electrochemical properties of one dimensional nanorods. The ability of MoO_2 to exhibit capacitive behaviour in the negative potential region makes the material a possible negative electrode for asymmetric hybrid electrochemical capacitors. This study on capacitive behaviour of MoO_2 nanorods suggests the possibility of considering them as alternates for the high cost RuO_2 electrodes.

Fig. 3. Galvanostatic charge–discharge curves of MoO_2 nanorods in 1 M H_2SO_4 at 1 mA cm^{-2} (solid line), 3 mA cm^{-2} (dotted line) and 5 mA cm^{-2} (dashed line).

References

[1] B.E. Conway, J. Electrochem. Soc. 138 (1991) 1539.
[2] R.F. Service, Science 313 (2006) 902.

[3] C.C. Hu, K.H. Chang, M.C. Lin, Y.T. Wu, Nano Lett. 6 (2006) 2690.
[4] W.C. Fang, O. Chyan, C.L. Sun, C.T. Wu, C.P. Chen, K.H. Chen, L.C. Chen, J.H. Huang, Electrochem. Commun. 9 (2007) 239.
[5] V. Srinivasan, J.W. Weidner, J. Electrochem. Soc. 144 (1997) L220.
[6] V.R. Shinde, S.B. Mahadik, T.P. Gujar, C.D. Lokhande, Appl. Surf. Sci. 252 (2006) 7487.
[7] S.Y. Wang, K.C. Ho, S.L. Kuo, N.L. Wu, J. Electrochem. Soc. 153 (2006) A75.
[8] R.N. Reddy, R.G. Reddy, J. Power Sources 156 (2006) 700.
[9] P. Simon, Y. Gogotsi, Nature Mater. 7 (2008) 845.
[10] A.S. Arico, P. Bruce, B. Scrosati, J.M. Tarascon, W.V. Schalkwihk, Nature Mater. 4 (2005) 366.
[11] C. Dekker, Phys. Today 52 (1999) 22.
[12] G.Y. Zhao, H.L. Li, Appl. Surf. Sci. 254 (2007) 3232.
[13] D.W. Kim, I.S. Hwang, S.J. Kwon, H.Y. Kang, K.S. Park, Y.J. Choi, K.J. Choi, J.G. Park, Nano Lett. 7 (2007) 3041.
[14] Y.R. Ahn, C.R. Park, S.M. Jo, D.Y. Kim, Appl. Phys. Lett. 90 (2007) 122106-1.
[15] H. Zhang, Y. Wang, E.R. Fachini, C.R. Cabrera, Electrochem. Solid-State Lett. 2 (1999) 437.
[16] A. Manthiram, C. Tsang, J. Electrochem. Soc. 143 (1996) L143.
[17] N.R. Elezovic, B.M. Babic, V.R. Radmilovic, S.Lj. Gojkovic, N.V. Krstajic, Lj.M. Vracar, J. Power Sources 175 (2008) 250.
[18] A. Vadivel Murugan, A. Kasi Viswanath, C.S. Gopinath, K. Vijayamohanan, J. Appl. Phys. 100 (2006) 074319-1.
[19] W. Sugimoto, T. Ohnuma, Y. Murakami, Y. Takasu, Electrochem. Solid-State Lett. 4 (2001) A145.
[20] Y. Takasu, T. Ohnuma, W. Sugimoto, Y. Murakami, Electrochemistry 67 (1999) 1187.
[21] A. Vadivel Murugan, A. Kasi Viswanath, G. Campet, C.S. Gopinath, K. Vijayamohanan, Appl. Phys. Lett. 87 (2005) 243511.
[22] B. Qi, X. Ni, D. Li, H. Zheng, Chem. Lett. 37 (2008) 336.
[23] J. Zhou, N.S. Xu, S.Z. Deng, J. Chen, J.C. She, Z.L. Wang, Adv. Mater. 15 (2003) 1835.
[24] B.C. Satishkumar, A. Govindaraj, M. Nath, C.N.R. Rao, J. Mater. Chem. 10 (2000) 2115.
[25] M.P. Zach, K.H. Ng, R.M. Penner, Science 290 (2000) 2120.
[26] R. Bowler, T.J. Davies, M.E. Hyde, R.G. Compton, Anal. Chem. 77 (2005) 1916.
[27] Y.R. Ma, C.C. Tsai, S.F. Lee, K.W. Cheng, J. Mag. Mag. Mater. 304 (2006) e13.
[28] J. Liu, Z. Zhang, C. Pan, Y. Zhao, X. Su, Y. Zhao, D. Yu, Mater. Lett. 58 (2004) 3812.
[29] L. Kumari, Y.R. Ma, C.C. Tsai, Y.W. Lin, S.Y. Wu, K.W. Cheng, Y. Liou, Nanotechnology 18 (2007) 115717(1).
[30] S.V. Pol, V.G. Pol, V.G. Kessler, G.A. Seisenbaeva, M. Sung, S. Asai, A. Gedanken, J. Phys. Chem. B 108 (2004) 6322.
[31] Y. Liang, Z. Yi, X. Lei, X. Ma, S. Yang, J. Sun, L. Yuan, Y. Zhou, J. Alloys Comp. 421 (2006) 133.
[32] J. Rajeswari, B. Viswanathan, T.K. Varadarajan, Mater. Chem. Phys. 106 (2007) 168.
[33] J. Rajeswari, P.S. Kishore, B. Viswanathan, T.K. Varadarajan, Nanoscale Res. Lett. 2 (2007) 496.
[34] M. Che, M. Fournier, J.P. Launay, J. Chem. Phys. 71 (1979) 1954.
[35] J.P. Zheng, T.R. Jow, J. Power Sources 62 (1996) 155.
[36] T. Morishita, Y. Soneda, H. Hatori, M. Inagaki, Electrochim. Acta 52 (2007) 2478.
[37] R.K. Selvan, I. Perelshtein, N. Perkas, A. Gedanken, J. Phys. Chem. C 112 (2008) 1825.
[38] S.B. Ma, K.W. Nam, W.S. Yoon, X.Q. Yang, K.Y. Ahn, K.H. Oh, K.B. Kim, Electrochem. Commun. 9 (2007) 2807.
[39] C.Z. Yuan, B. Gao, X.G. Zhang, J. Power Sources 173 (2007) 600.