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Multiwalled Carbon Nanotubes beaded with Nickel Molybdate for superior electrochemical characteristics

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Abstract. NiMoO₄ were synthesised on multiwalled carbon nanotubes (MWCNTs) via a simple and environment-friendly solvothermal method. The nanostructures were interconnected forming a sponge-like network providing a large surface area easily accessible to electrons and ion during intercalation-deintercalation process. The MWCNT/NiMoO₄ nanocomposite exhibited a specific capacitance of 455 F/g at 4 A/g as an electrode material for an electrochemical capacitor and 66 % of its initial capacitance was retained after 1000 cycle. This study presented a research strategy for developing ternary based electrode material for electrochemical capacitors.

1. Introduction

NiMoO₄ as a binary transition metal oxide belonging to the metal-molybdate family has drawn advances in research due to its remarkable electrochemical activity in terms of chemical stability, abundant reserve, low cost and environmental benignity for its use as an electrode material for electrochemical capacitors [1]. Nevertheless, the poor electrical conductivity and cycling stability of metal oxides limits its specific capacitance [2]. To improve this drawback, the integration of carbon materials provide accessible electroactive sites, rapid electron-transport and an attractive synergetic characteristics which can deliver better electrochemical performance [2,3].

The open mesoporous network of carbon nanotubes (CNTs) allows easy ion diffusion to the active surface of the nanocomposite electrodes coupled with the high resiliency of the nanotubes to easily adapt to the volumetric changes during the charge and discharge process. These features of CNTs including its high conductivity, largely accessible surface area and its double layer capacitance improve the overall electrochemical performance of the CNT/metal oxide nanocomposite representing an essential factor for developing the next generation electrochemical capacitors [4]. In this study, we incorporate a facile solvothermal approach for the synthesis of the MWCNT/NiMoO₄ ternary nanocomposites. The structural and electrochemical properties of the MWCNT/NiMoO₄ metal oxide ternary composite used as electrodes



for electrochemical capacitors were analysed comprehensively. Furthermore, different weight ratios of MWCNT to NiMoO₄ were prepared and their electrochemical performance evaluated respectively.

2. Experimental

2.1. Synthesis of the multi-walled carbon nanotubes

Using the water assisted catalytic chemical vapor deposition (CCVD) growth method, multi-walled carbon nanotubes were produced in quartz tube furnace. Ethylene (40–400 sccm) was mixed hydrogen (30-150sccm) before being diluted with argon (100-350sccm). Water was added continuously in the chamber by refluxing Ar (5-50sccm) using a water bubbler. Fe (1nm) deposited on a silicon substrate and additional Al₂O₃ (10nm) as top layer was used as the catalyst. Before the process, the furnace temperature was set at 750°C and the substrate was used for the growth of the multi-walled carbon nanotubes.

2.2. Synthesis of MWCNTs/NiMoO₄ ternary composites

0.29g of MWCNTs was dispersed in a solution of ethanol and water at an apt ratio (2:3) by sonication for 20 minutes. A different mixture of 0.29g of nickel (II) nitrate hexahydrate and with 0.24g of sodium molybdate was prepared in 30 ml of deionized water under stirring. The later solution was then added to the MWCNT solution under stirring for 15 minutes to achieve homogeneity. The solution was transferred into a 50 ml Teflon autoclave and heated to 160°C for 6 hours. The precipitate collected was washed thoroughly and dried overnight. The dried composites were calcined at 400°C for 4 hours. Ratios (1:1, 1:4, 1:8 and 1:16) of MWCNTs to NiMoO₄ were prepared and labeled MWCNT-NM, MWCNT-4NM, MWCNT-8NM and MWCNT-16NM respectively

2.3. Characterization

The X-ray diffraction (XRD, Bruker D4) pattern of the nanocomposites are recorded from 10 to 70 ° using Cu-K α radiation ($\lambda=1.54056 \text{ \AA}$) with step size 0.03. The Raman spectra were measured on a Raman spectrometer (Renishaw inVia Raman microscope) with a diode laser excitation source of 532 nm and a CCD detector. The surface characteristics of the nanocomposites were investigated using a Field electron scanning electron microscope (FE-SEM, FEI Quanta-400 FE-SEM) with an EDX analyser and a (TEM, JEOL JEM-2100F) at an operating voltage of 200 kV.

The working electrodes were fabricated from a mixture of 70 wt% MWCNT/NiMoO₄ composites, 20 wt% carbon black and 10 wt% polyvinylidene fluoride (PVDF). The electrodes weighting about 1 mg were tested in a two electrode cell using 2 M KOH solution on an Arbin Instrument (BT-2000) and Metrohm Autolab (PGSTAT302F) electrochemical working stations.

3. Results and discussion

The diffraction peaks of MWCNT/NiMoO₄ and NiMoO₄ (Figure 1) can be indexed to α -phase NiMoO₄ with JCPDS card no 086-0361 [5]. The peak at about 26.6° and 44.4° observed in the CNT/NiMoO₄ composites can be attributed to the (002) and (101) reflection of carbon respectively. These peaks almost overlaps with the (-112) and (330) peaks of NiMoO₄ at a low concentration of MWCNT which makes it challenging to identify.

Energy dispersive X-ray (EDX) analysis depicts the element signals of C, Ni, Mo, and O seen in the spectrum (Figure 2a). The element Si is due to the silicon substrate used during characterization. The Raman spectrum of MWCNT/NiMoO₄ composites (Figure 2b) displays the typical carbon peaks located at the 1346 cm⁻¹ (D band), 1574 cm⁻¹ (G band) and 2688 cm⁻¹ (2D band) respectively [6]. The other peaks at 946, 899, 816, 701, 382 and 245 cm⁻¹ respectively can be attributed to the α -phase NiMoO₄ as reported in literatures [7].

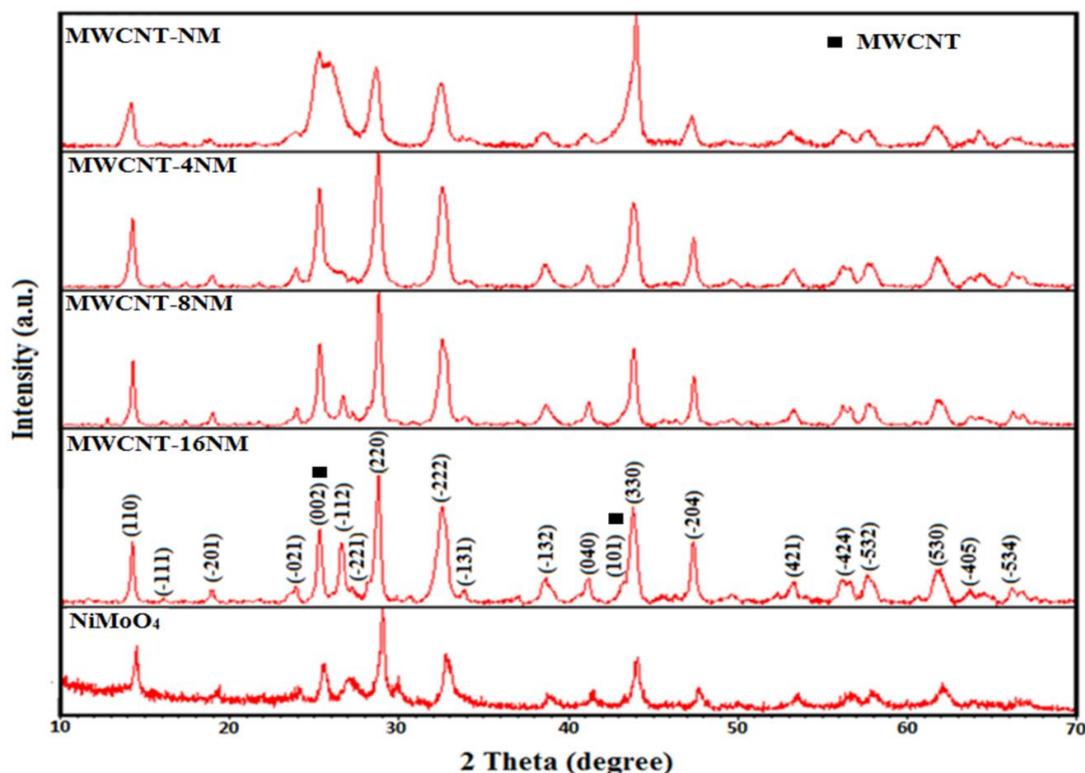


Figure 1: XRD pattern of NiMoO₄ and CNT-NiMoO₄ composites.

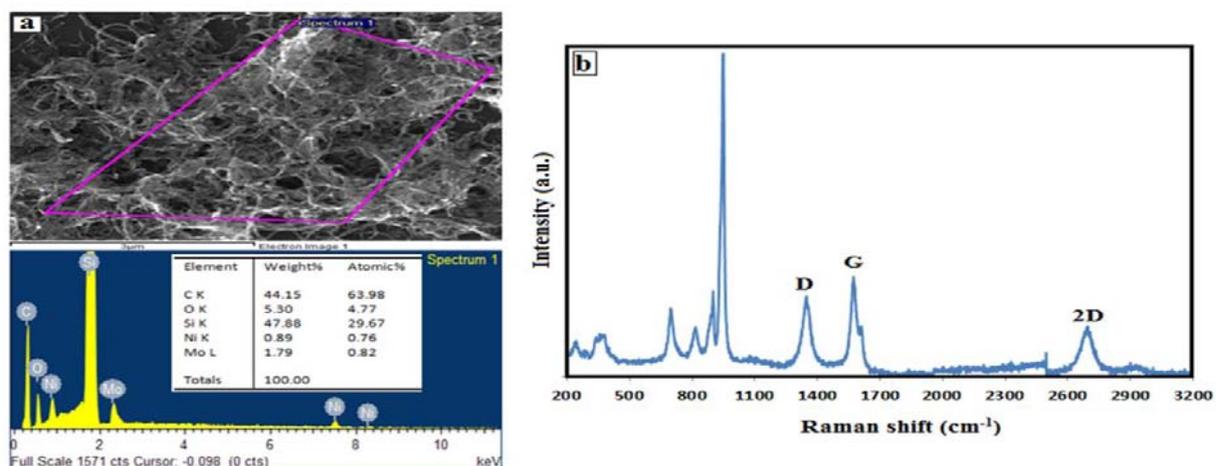


Figure 2: Images of (a) EDX spectrum and (b) Raman spectrum of MWCNT-NiMoO₄ composites respectively.

The morphology of the CNTs, the CNT/NiMoO₄ composites was investigated by FE-SEM and TEM as shown in figure 3. It can be observed in Figure 3a that the diameter of the MWCNTs is about 30 to 50 nm. Figure 3 (b-e), confirms that the solvothermal synthesis was successfully carried out with the NiMoO₄ rods inter connected with MWCNTs forming a sponge-like structure. The concentric layers can be easily in the HRTEM image (figure 3f) and with lattice fringes of 0.34 nm correlating with the (220) reflection of NiMoO₄

in the XRD study. Figure 4a depicts the cyclic voltammograms (CV) curves of the MWCNT-NiMoO₄ composites and NiMoO₄ electrodes at a scan rate of 30 mV/s⁻¹. The redox peaks seen in each curve can be attributed to the reversible faradaic process of Ni²⁺/Ni³⁺ [8]. Compared with NiMoO₄, the nanocomposite electrodes exhibited higher integrated area under the curve implying better charge transfer due to the double layer capacitance and pseudocapacitance resulting from the MWCNT and NiMoO₄ respectively. At different scan rates of the MWCNT-4NM electrode (figure 4b), the shape of the curves were not significantly influenced indicating good rate capability and reversibility of the electrode. Charge/discharge analysis were performed on the electrodes at current density of 4 A/g. The MWCNT-4NM electrode displayed the longest discharge time signifying that the electrode having the best charge storage ability and this evident of the specific capacitances calculated from the discharge curves (figure 4c) to be NiMoO₄ (166 F/g), MWCNT-NM (280 F/g), MWCNT-4NM (455 F/g), MWCNT-8NM (397 F/g) and MWCNT-16NM (267 F/g) respectively. Notably, the highest capacitance was achieved via the optimal mixture of MWCNT: NiMoO₄ = 1:4, in which this combination provided the best synergistic effect between the high electrical conductivity of CNT and the high pseudocapacitance of the metal oxide.

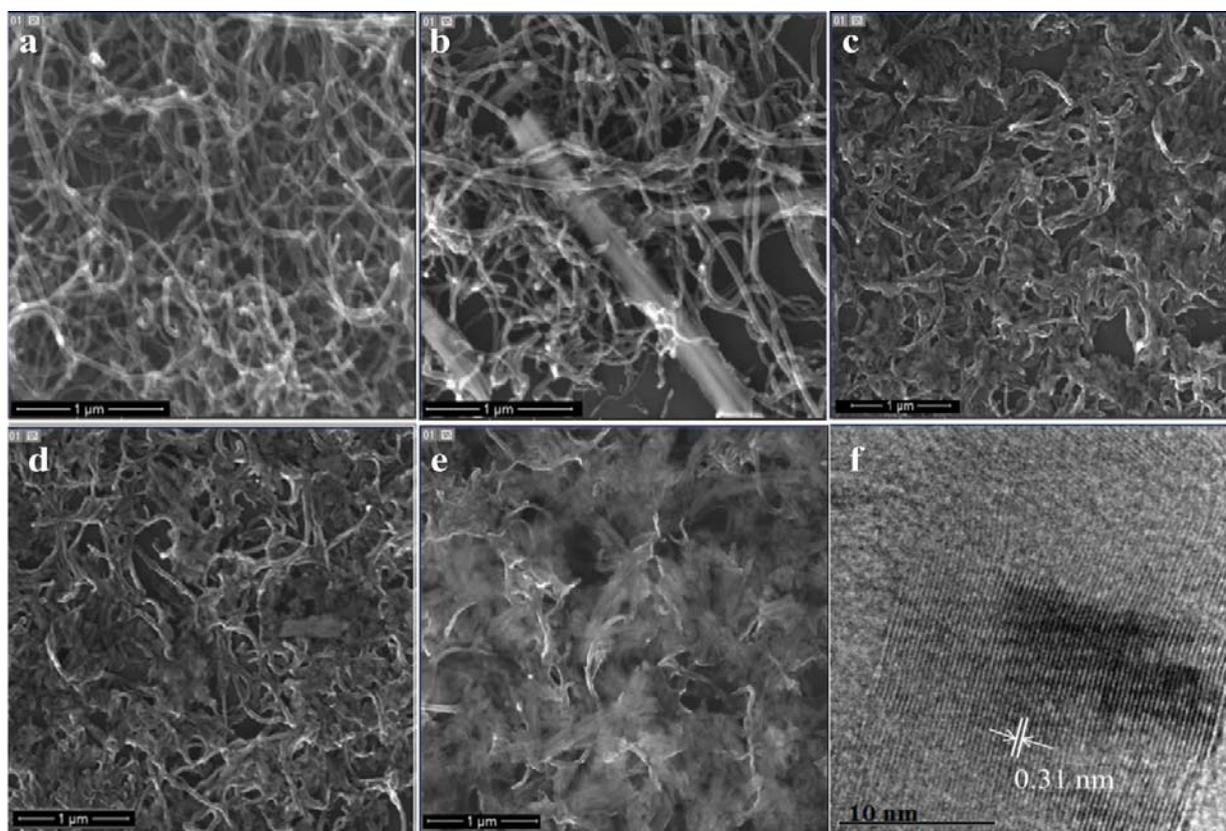


Figure 3: FE-SEM images of (a) MWCNT, (b) MWCNT-NM, (c) MWCNT-4NM, (d) MWCNT-8NM (e) MWCNT-16NM and (f) HRTEM image of CNT-NiMoO₄ nanocomposites.

At different current densities (figure 4d), there were no immense changes in the charge/discharge curves of the MWCNT-4NM electrode implying good rate capability and reversibility as seen in figure 4b. The stability of the MWCNT-4NM electrode was measured at a current density of 3 A/g between 0 – 1 V (figure 4e) and 66 % of its initial capacitance were retained after 2000 cycles. Figure 4f displays the EIS of the composite electrodes; all the curves exhibited a semi-circle at high frequency and a linear component at low-frequency. The semi-circle indicates low charge transfer resistance (R_{ct}); MWCNT-4NM electrode having the smallest (R_{ct}) is in agreement with other electrochemical performances recorded. This performance is

mainly due to the large surface area exploited by the NiMoO₄ pseudocapacitance and MWCNT double-layer capacitance [9].

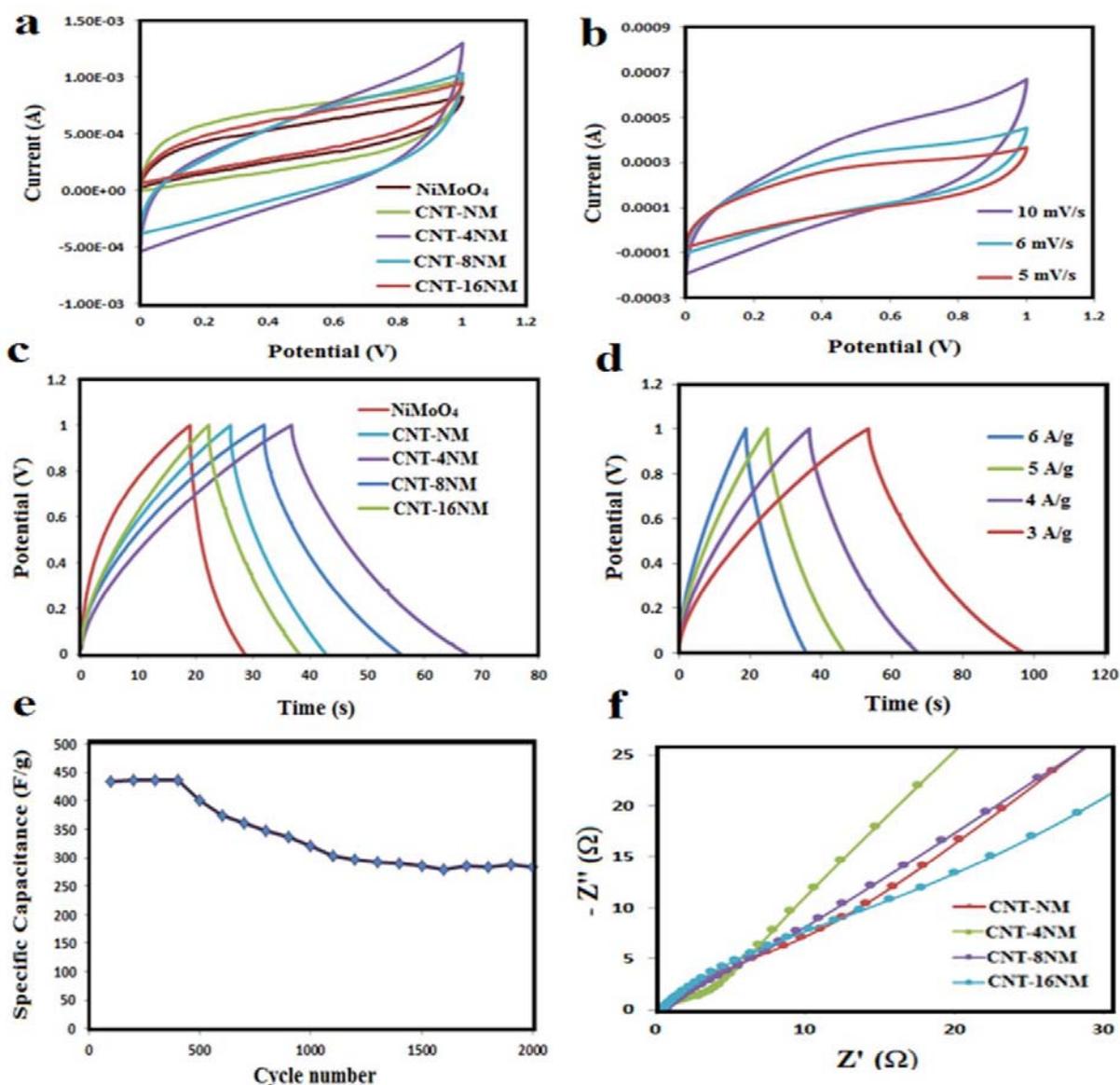


Figure 4: CV curves of (a) NiMoO₄, MWCNT-NM, MWCNT-4NM, MWCNT-8NM and MWCNT-16NM at a scan rate of 30 mV/s, (b) MWCNT-4NM electrode at different scan rates ranging from 5-10 mV/s, (c) Charge-discharge curves of NiMoO₄, MWCNT-NM, MWCNT-4NM, MWCNT-8NM and MWCNT-16NM at a current density of 4 A/g (d) Charge-discharge curves of MWCNT-4NM at different current densities (e) cycle life of the MWCNT-4NM electrode at a current density of 3 A/g (f) Nyquist plot of the MWCNT-NM, MWCNT-4NM, MWCNT-8NM and MWCNT-16NM composites electrodes.

4. Conclusion

MWCNT-NiMoO₄ nanocomposites were successfully synthesised by a facile solvothermal method. The combination of carbon nanotubes and metal oxides complements each other in terms of conductivity and pseudocapacitance. The MWCNT-NiMoO₄ composite electrodes exhibited capacitance of 455 F/g at 3 A/g

with excellent rate capability. This strategy provides a promising electrode material for electrochemical capacitors.

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References

- [1] Xiao K, Xia L, Liu G, Wang S, Ding L X, and Wang H 2015 *J. Mater. Chem. A* **3** 6128–35.
- [2] Guo D, Luo Y, Yu X, Li Q, and Wang T 2014 *Nano Energy* **8** 174–182.
- [3] Liu T, Chai H, Jia D, Su Y, Wang T, and Zhou W 2015 *Electrochim. Acta* **180** 998–1006.
- [4] Pan H, Li J, and Feng Y 2010 *Nanoscale Res. Lett.* **5** 654–668.
- [5] Jothi P R, Kannan S, and Velayutham G 2015 *J. Power Sources* **277** 350–9.
- [6] Xia H, Wang Y, Lin J, and Lu L 2012 *Nanoscale Res. Lett.* **7** 33
- [7] Abdel-Dayem H M 2007 *Ind. Eng. Chem. Res.* **46** 2466–72.
- [8] Wan H, Jiang J, Ji X, Miao L, Zhang L, Xu K, Chen H, and Ruan Y 2013 *Mater. Lett.* **108** 164–7.
- [9] He G, Wang L, Chen H, Sun X, and Wang X 2013 *Mater. Lett.* **98** 164–7.