



Capacitive performance of molybdenum nitride/titanium nitride nanotube array for supercapacitor



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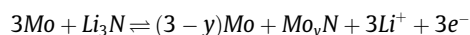
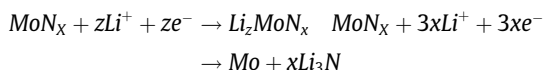
ABSTRACT

Molybdenum nitride (MoN_x) depositing on titanium nitride nanotube array (TiN NTA) was designed as MoN_x/TiN NTA for supercapacitor electrode material. MoN_x/TiN NTA was fabricated by electrodepositing molybdenum oxide onto titanium dioxide NTA and one-step nitridation treatment in ammonia. MoN_x/TiN NTA involved top-surface layer of MoN_x nanoparticles and underlying layer of TiN NTA, which contributed to electric double layer capacitance in aqueous lithium-ion electrolyte solution. The specific capacitance was increased from 69.05 mF cm^{-2} for TiN NTA to $121.50 \text{ mF cm}^{-2}$ for MoN_x/TiN NTA at 0.3 mA cm^{-2} , presenting the improved capacitance performance. MoN_x exhibited the capacitance of 174.83 F g^{-1} at 1.5 A g^{-1} and slightly declined to 109.13 F g^{-1} at 30 A g^{-1} , presenting high rate capability. MoN_x/TiN NTA exhibited the capacitance retention ratio of 93.8% at 3.0 mA cm^{-2} after 1000 cycles, presenting high cycling stability. MoN_x/TiN NTA could act as a promising electrode material of supercapacitor.

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1. Introduction

Supercapacitors with high power density, high cycling life and reasonable energy density could be applied for new energy field. The suitable electroactive materials become the key factor to construct high-performance supercapacitors [1,2]. In recent years, molybdenum nitride (MoN_x) has been used as active electrode material owing to its high electrochemical activity, chemical stability, good electrical conductivity above 0.2 S cm^{-1} and good resistance to electrochemical decomposition in aqueous electrolytes [3–6]. The energy storage mechanisms of MoN_x mainly relies on the different electrochemical processes in different electrolyte solutions and the applied potential ranges, which involves the electric double-layer capacitance and Faradaic pseudocapacitance [7]. Electroactive MoN_x such as $\gamma\text{-Mo}_2\text{N}$ has the layered crystal structure to achieve effective charge storage capability [8–11]. The layered MoN_x has been investigated as an anode material in lithium-ion batteries, conducting reversible intercalation/deintercalation of lithium-ion in lithium-ion contained organic solution [8,12].



The initial lithium-ion intercalation reaction of MoN_x causing to form Li_zMoN_x takes place at 1.2 V vs Li/Li^+ . The followed conversion reaction of MoN_x with lithium-ion causing to form Li_3N takes place at 0.4 V vs Li/Li^+ [13]. The reversible oxidation and reduction reaction of Li_3N in the charge/discharge process takes place at 1.5 and 2.5 V vs Li/Li^+ [8]. The MoN_x has also been investigated as electrode materials of supercapacitors. MoN_x involved the pseudocapacitance performance in protonic electrolyte solution through reversible intercalation/deintercalation of proton and electric double-layer capacitance in aqueous electrolyte solution through reversible adsorption/desorption of reactive ion [9,10]. In view of electrode substrate materials, the various carbon materials have been applied as the supporting substrates of supercapacitors [14,15]. Alternatively, titanium nitride nanotube array (TiN NTA) has attracted more and more interests due to its chemical stability and high conductivity [11,16]. The electrochemical applications of TiN NTA have been investigated [17–19]. The tubular channels of three-dimensional TiN NTA have large surface area, benefiting for ion diffusion and electron transport capability of active materials [20–22].

In this study, MoN_x/TiN NTA was fabricated by one-step nitridation of $\text{MoO}_x/\text{TiO}_2$ NTA in ammonia atmosphere. Considering the less dissolution of molybdenum ion in alkaline solution rather than acidic solution, MoN_x has much lower leakage current in alkaline electrolyte solution [23]. Lithium hydroxide is accordingly used

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as a reactive electrolyte of MoN_x/TiN electrode material. Generally, the layered MoN_x/TiN NTA shows much higher capacitance than graphite carbon and much higher conductivity than lithium transition-metal oxide. Conductive TiN NTA with well-aligned nanotubular structure could provide electric double layer capacitance and enhance the electron transmission capability of MoN_x . Electroactive MoN_x with a layered structure could contribute to feasible electrochemical reaction in LiOH solution. MoN_x/TiN NTA is expected to have an improved capacitance performance for supercapacitor application.

2. Experimental

2.1. Fabrication of MoN_x/TiN NTA

Fig. 1 illustrates the fabricating process of MoN_x/TiN NTA. TiO_2 NTA was formed by anodizing metallic Ti foil. Subsequently, MoO_x was electrodeposited on TiO_2 NTA in 0.003 M ammonium molybdate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$) solution to prepare $\text{MoO}_x/\text{TiO}_2$ NTA. The electrodeposition reaction was conducted for 20 min at a scan rate of 50 mV s^{-1} and a potential range from -0.75 V to 0 V . Finally, $\text{MoO}_x/\text{TiO}_2$ NTA was converted to MoN_x/TiN NTA by one-step nitridation process. The pre-nitridation treatment was conducted through a controlled temperature-rise program from 700 to $900 \text{ }^\circ\text{C}$ with an increase rate of $1 \text{ }^\circ\text{C min}^{-1}$. Then, the steady nitridation process could be achieved through an annealing treatment at $900 \text{ }^\circ\text{C}$ for 2 h.

2.2. Characterization and measurement

The morphology and microstructure of MoN_x/TiN NTA was investigated by Zeiss Ultra-Plus scanning electron microscope (SEM) with an electron beam energy of 20 keV . The element composition of samples was investigated through energy dispersive X-ray (EDX) measurement using the Zeiss Ultra Plus equipped with an Oxford ISIS 310 detector at an accelerating voltage of 20 kV . Crystal structure was investigated through X-ray diffraction (XRD) measurement using a Philips PW3020 diffractometer fitted with a graphite monochromator. An accelerating voltage of 40 kV and a current of 30 mA were used to produce Cu K_α radiation at a wavelength of 0.15418 nm . All electrochemical measurements were performed using a three-electrode system in one testing cell, which includes a working electrode, the saturated calomel electrode as a reference electrode, the platinum foil as an auxiliary

electrode and 1.0 M LiOH electrolyte solution. The cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) measurements were carried out using a CHI760D electrochemical workstation at a controlled potential window, scan rate and current density. Electrochemical impedance spectroscopy (EIS) measurement was carried out using an IM6e electrochemical workstation at an open-circuit voltage of 0.6 V , a disturbing voltage of 5 mV and a frequency range of $0.01\text{--}100 \text{ kHz}$.

3. Results and discussion

3.1. Structure characterization

XRD analysis was conducted to determine crystal phase of MoN_x/TiN NTA. Fig. 2 shows the XRD patterns of MoN_x/TiN NTA and TiN NTA. The diffraction peaks at 37.2° , 39.3° , 41.3° , 52.8° , 64.1° , 70.5° and 75.3° were ascribed to lattice planes (0 0 2), (1 0 1), (0 1 1), (1 0 2), (1 1 0), (1 0 3) and (1 1 2) of metallic crystal Ti (JCPDS 01-089-5009). Herein, as-formed MoN_x/TiN NTA was directly grown and supported on Ti foil substrate. The presence of titanium metal crystal phase in addition to TiN and MoN_x crystal phases was attributed to the Ti foil substrate. The diffraction peaks at 36.2° , 43.3° , 54.5° and 61.5° were ascribed to lattice planes of (1 1 1), (2 0 0), (1 0 1) and (2 2 0) of TiN (JCPDS 00-038-1420). As-formed TiN NTA could be indexed to cubic crystal phase. Comparatively, in addition to above characteristic peaks of TiN and Ti, other new diffraction peaks could be observed in MoN_x/TiN NTA. The overlapped and independent diffraction peaks at 37.3° , 43.6° , 48.1° , 64.1° , 75.3° and 77.8° were ascribed to lattice planes of (1 1 2), (2 0 0), (2 1 0), (2 2 0), (3 1 1) and (2 2 2) of MoN_x . As-formed MoN_x could be mainly assigned to bulk cubic crystal $\gamma\text{-Mo}_2\text{N}$ (JCPDS 00-025-1366) along with few Mo_3N_2 (JCPDS 01-089-5025) [8,10,11]. The $\gamma\text{-Mo}_2\text{N}$ has the typical layered crystal structure where the intercalation location is the octahedral sites and tetrahedral sites [9]. It indicates that the initially formed $\text{MoO}_x/\text{TiO}_2$ could be converted into the ultimate MoN_x/TiN NTA through the controlled one-step nitridation process [24].

EDX analysis was conducted to further confirm the conversion from $\text{MoO}_x/\text{TiO}_2$ NTA to MoN_x/TiN NTA through identifying element composition. Fig. 3 (A) shows EDX patterns of MoN_x/TiN NTA supporting on Ti foil. The energy dispersive peaks at 0.42 , 4.52 , and 4.94 keV were ascribed to titanium element. The energy dispersive peak at 0.42 keV was also ascribed to nitrogen element. The energy dispersive peaks at 2.28 and 2.78 keV were ascribed to molybdenum element. The mass ratio of molybdenum and

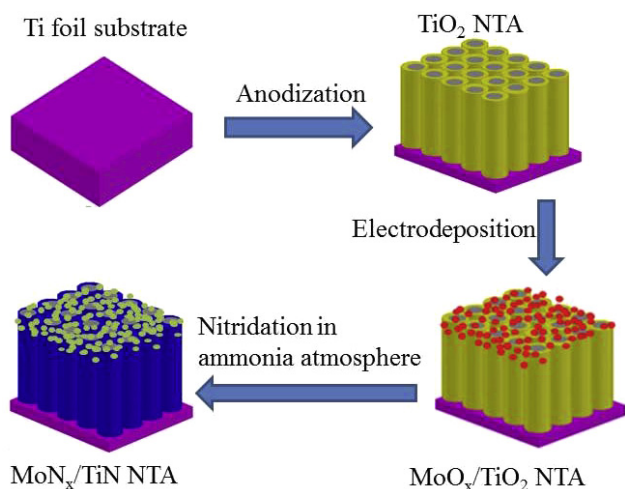


Fig. 1. A schematic showing the fabrication process of MoN_x/TiN NTA.

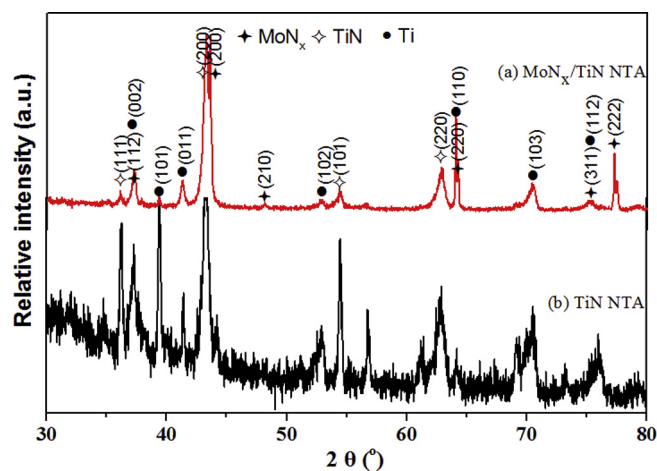


Fig. 2. XRD patterns of MoN_x/TiN NTA and TiN NTA supporting on Ti substrate.

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