Fabrication and Application of Molybdenum Trioxide Nanostructure Materials for Electrochemical Capacitors

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In this paper, a new method of “top-down” metal-assisted chemical wet etching to fabricate MoO₃ nanostructure materials is put forward for the first time by the authors, which overcomes the weakness such as complex technology and high cost. In the solution system of AgNO₃/ HNO₃, the fabrication of MoO₃ nanostructure materials is conducted under certain conditions and then the samples are annealed under high temperature as 500 - 700 ℃. Observed by scanning electron microscope (SEM), when the concentration of AgNO₃ is 0.01 M, HNO₃ solution concentration as 3.6 M, the temperature as (20 ± 2) ℃, the etching time as 90 min, the anneal temperature as 600 ℃, the fabricated MoO₃ nanostructure materials has well morphology. In 0.5 M Na₂SO₄ solution, the sample electrode (600 ℃) shows a higher capacitance of 30.85 F g⁻¹ at 10 mV / s. The method above to fabricate MoO₃ owns the superiority such as simple, low cost and easy to control the reaction process, so it will be popularized for large-scale fabrication of MoO₃ nanostructure materials.

Keywords: Molybdenum trioxide nanostructure materials; Metal-assisted chemical etching; Top-down method; Electrochemical capacitors

1. INTRODUCTION

Currently the preparation of Molybdenum trioxide (MoO₃) nanostructure materials is limited to a “bottom-up” method, for example, pulsed laser deposition method (PLD), gas phase method, chemical precipitation method, etc. They have some disadvantages such as expensive, difficult to prepare and rigorous environmental requirements. MoO₃ has good gas-sensitive properties, photosensitive properties, photochromic and electrochemical properties [1-3]. It has an important application in such as gas sensors, optical switching devices, a new type of energy storage device, image display,
information storage, variable reflectivity lens and efficient smart windows, being the research focus of nanometer metal oxides [4-6].

MoO$_3$ is an attractive example of bright prospect anode and cathode materials for electrochemical capacitor due to its unique layered structure [7]. However, nowadays the preparation of MoO$_2$/MoO$_3$ nanostructure materials is limited to chemical precipitation method, hydrothermal method, sol-gel method, gas phase method, etc., which are based on MoO$_3$ powder, Na$_2$MoO$_4$ and (NH$_4$)$_2$MoO$_4$ [8-10]. All of above methods require high temperature and strong pressure, so the cost of manufacturing becomes larger. We need low-cost, high-volume molybdenum trioxide nanostructure materials manufacturing process.

In recent years, research on electrochemical capacitors relation with molybdenum oxide triggers a boom [11]. Electrochemical capacitors are widely used as superior energy storage devices, which own higher power density than traditional batteries and energy density than electrostatic capacitors. D. S. Guan et.al coating MoO$_3$ on TiO$_2$ nanotubes exhibit a capacitance up to 74.9 F g$^{-1}$ at 5 mV / s in 1 M KCl solution [12]. I. Shakir et.al synthesized MoO$_3$ nanowires by dissolving MoO$_2$ in H$_2$O$_2$ and mixing SnCl$_2$ with MoO$_3$ to fabricate MoO$_3$ nanowires decorating with SnO$_2$ in order to get super capacitor performance [13]. So we can conclude that decorating MoO$_3$ nanostructure materials with metal oxide such as TiO$_2$, SnO$_2$, NiO will improve capacitance of electrochemical capacitor.

In this paper, a method of metal-assisted wet etching to obtain molybdenum oxide nanostructure materials is proposed. Adopting AgNO$_3$/HNO$_3$ solution system is a groundbreaking method to grow nanostructure of molybdenum oxide. Thermal treatment will contribute to finish the translation from MoO$_x$ to MoO$_3$. At the same time, the electrochemical properties had been detected, the results show the nanocomposites have better electrochemical capacitance characteristics is a promising electrode material in electrochemical capacitors.

2. METHODS

Molybdenum foils (>99.99%) were cut into 2 cm * 1 cm * 0.1 cm. Chemical reagents such as AgNO$_3$, HNO$_3$ (65%-68%), NaOH, acetone, absolute ethyl alcohol, deionized water, silver paste and epoxy resin were used as-received without any processing.

There are three steps during molybdenum foils pretreatment. Firstly, the molybdenum foils’ specifications was 2 cm * 1 cm * 0.1 cm and then to planish it.

Secondly, KQ-100DV CNC ultrasonic cleaner for five-step cleaning molybdenum foils, order: deionized water (time: 5 min), acetone (time: 5 min), deionized water (time: 5 min), 1 M NaOH solution (time: 5 min), deionized water (time: 5 min). Then dry it under room temperature.

Thirdly, after the five-step cleaning, to rinse the molybdenum foil with flowing deionized water, then removed and reserved.

In this experiment, concentrations of HNO$_3$ and AgNO$_3$ varied so that their influence on the formation of MoO$_2$ nanostructure materials could be distinguished. In order to explore the effect of HNO$_3$, we fixed the AgNO$_3$ concentrations and change the concentrations of HNO$_3$, and the concentration was varied from 1.8 M to 14.4 M. To explore the effect of AgNO$_3$, we fixed the HNO$_3$
concentrations and change the concentrations of AgNO₃, and the concentration was varied from 0.01 M to 0.08 M. The concentration ladder was 0.01 M. All of that were preparations under normal conditions (room temperature 20 ± 5 °C, 1 atmosphere pressure (1 atm)).

The cleaned molybdenum foils were first put into the beakers with different HNO₃ and AgNO₃ concentrations. The etching process was maintained under normal conditions. At first, the appropriate HNO₃ and AgNO₃ concentrations were chosen, so the next point was to find the proper temperature and time. We varied the temperature and time from -20 °C to 60 °C and 30 min to 120 min respectively. After the MoOₓ nanostructure materials preparation, some samples were rinsed with 1.8 M HNO₃ to remove the redundant Ag. After drying at room temperature, to anneal it in a tube furnace at 500 °C, 600 °C and 700 °C for 2 h, 10 °C/ min.

The morphologies of prepared samples were observed by Scanning Electron Microscopy (SEM, Hitachi S-4300). Elemental composition analysis was conducted by Energy Dispersive Spectrometer (EDS, Hitachi S-4300). X-ray Photoelectron Spectroscopy (XPS) was operated on ESCALAB 250Xi (Thermo Fisher, USA). Electrochemical properties measurements were performed with electrochemical workstation (CHI 604e, Chen Hua of Shanghai). The three-electrode system was composed of a reference electrode (Ag / AgCl), a counter electrode (Pt) and the working electrode (sample electrode).

3. RESULTS AND DISCUSSION

Under the normal conditions, the influence parameters were the concentration of HNO₃, the concentration of AgNO₃, temperature and etching time. In this section, these parameters were investigated independently. In this metal-assisted etching reaction system, Ag⁺ obtained electrons while Mo lost electrons. Moreover, Ag was not stable in the solution of HNO₃ and translated to Ag⁺ soon. After repeated experiments, we confirmed the value of the influence parameters, detailed process as follows.

In the first group of the experiment, we set the concentration of AgNO₃ at 0.01 M, temperature at 20 °C for 90 min. The concentration of HNO₃ was 1.8 M, 2.4 M, 3.6 M, 5.4 M, 7.2 M, 10.8 M and 14.4 M respectively. At the start of the experiment, beaker of 1.8 M almost had no reaction (very slight at first, the foil turned to black 30 minutes later), which could be attributed to the lowest concentration. The beaker of 14.4 M did not change too, which could be attributed to molybdenum foils reacted nothing in saturation HNO₃ under room temperature. The remainder five beakers, except lowest and highest one, reaction intensity was rising in turn. Taking into account of environmental friendliness and cost, we chose the concentration of HNO₃ as 3.6 M.

In the second group of the experiment, we set the concentration of HNO₃ at 3.6 M, temperature at 20 °C for 90 min. The concentration of AgNO₃ was 0.01 M, 0.02 M, 0.03 M, 0.04 M, 0.05 M, 0.06 M, 0.07 M and 0.08 M respectively. All of the samples react at the same time, and etching appearance was so similar that we concluded the concentration of AgNO₃ had little effect, which let us chose 0.01 M.
In the third group of the experiment, we set the concentration of HNO$_3$ at 3.6 M, the concentration of AgNO$_3$ was 0.01 M, and time was 90 min. The temperature was -20 °C, -10 °C, 10 °C, 20 °C, 30 °C, 40 °C, 50 °C and 60 °C respectively. The higher the temperature was, the stronger the reaction would be. However, once the temperature was too high, it would get the opposite effect. Molecular movement was too violent to obtain regular appearance and structure, choosing 20 °C as the most appropriate temperature.

In the fourth group of the experiment, we set the concentration of HNO$_3$ at 3.6 M, the concentration of AgNO$_3$ as 0.01 M, and temperature at 20 °C. Time was 30 min, 60 min, 90 min, 120 min. The etching time would affect deepness of sample, so it was significant to control time to obtain the best sample we wanted. 30 min was so short that we could not get etching hole we needed. The sample of 60 min was much better than 30 min but etching pattern was worse than the sample of 90 min. 120 min was too long to get proper pattern. In most of our experiment, we always chose 90 min.

**Figure 1.** SEM sample—(a) molybdenum foil under etching; (b) upper surface ×1000; (c) fracture surface ×100000; (d) the upper surface of split-block ×5000

In a word, we chose the concentration of HNO$_3$ is 3.6 M, the concentration of AgNO$_3$ is 0.01 M, temperature is 20 °C and etching time is 90 min, fabricating the sample we needed. Fig.1a described the initial molybdenum foil, turning black in etching solution and generating bubble during entire etching progress. Fig.1b revealed the initial etching sample after etching under SEM. Crack was obvious on the upper surface of the sample, and its formation was natural for existence of HNO$_3$. Fig.1c revealed fracture surface of sample, and nanostructured particle was formation during the reaction. To some extent, Mo was protected by Ag, on which Ag$^+$ covering. Just as Fig.1d shown, several Ag nanoparticles were on the surface of split-block. The reaction chemical equation as follows:
\[
\text{Ag}^+ + e^- \rightarrow \text{Ag}
\]
\[
3\text{Ag} + 4\text{HNO}_3 \rightarrow 3\text{AgNO}_3 + \text{NO}↑ + 2\text{H}_2\text{O}
\]

The chemical equation above can explain the pungent gas that generated during etching. Ag / Ag\textsuperscript{+} translation was in an endless cycle until the consumption of molybdenum. In this way, AgNO\textsubscript{3} could be recycled that could also save cost.

The valence of Mo during etching was uncertain. Mo replaced Ag in solution, losing electronics and changing to Mo\textsuperscript{4+}, Mo\textsuperscript{5+} or Mo\textsuperscript{6+}. MoO\textsubscript{x} is extremely hardly dissolved in HNO\textsubscript{3}, so it could exist in a short time. The percentage of MoO\textsubscript{x} was extremely little for the existence of HNO\textsubscript{3}. In order to obtain more stable MoO\textsubscript{3}, we put samples into a tube furnace for 2 hours. Mo-Mo band was destroyed companying with Mo-O band occurring, which made the surface of molybdenum go black as Fig. 1a.

\[
\text{Mo} - 6e^- \rightarrow \text{Mo}^{6+}
\]
\[
\text{Mo} - 5e^- \rightarrow \text{Mo}^{5+}
\]
\[
\text{Mo} - 4e^- \rightarrow \text{Mo}^{4+}
\]
\[
\text{Mo}^{5+} + e^- \rightarrow \text{Mo}^{4+}
\]
\[
\text{Mo} + 4\text{H}_2\text{O} \rightarrow \text{H}_2\text{MoO}_4 + 6\text{H}^+ + 6e^-
\]
\[
\text{H}_2\text{MoO}_4 + 2\text{H}^+ + 2e^- \rightarrow \text{MoO}_2\text{ (s)} + 3\text{H}_2\text{O}
\]
\[
\text{MoO}_2\text{ (s)} + 4\text{H}^+ + 4e^- \rightarrow \text{Mo}\text{ (s)} + 2\text{H}_2\text{O}
\]

Energy Dispersive Spectrometer (EDS) was used to analyze composition on the surface of sample. The purity of molybdenum foil was 99.99 %, which signified that there may contain other elements such as lead, tungsten, platinum and so on. However, they could be negligible because they neither reacted with oxygen nor changed the valence of Molybdenum. A small quantity of silver was residual during etching process, which would be removed by diluent HNO\textsubscript{3} easily.

Figure 2. EDS sample—after etching (Range unit: keV)
Fig. 2 displayed that the weight percentage of Oxygen was only 5.41% and we could surmise that a few Molybdenum was oxidized during etching. In order to obtain much more Oxygen and get stable crystalline phase structure, we took thermal annealing treatment.

![Figure 3. SEM sample—anneal at 500°C for 2h, 10°C/min (a) upper surface -×500; (b) upper surface -×10000](image)

![Figure 4. SEM sample—anneal at 600°C for 2h, 10°C/min (a) upper surface -×500; (b) upper surface -×10000; (c) surface of crystal orientation (012)](image)

In order to obtain more stable nanostructure MoO$_3$, 500 - 700°C anneal temperature was adopted. Mo could be oxidized to MoO$_2$ above 350°C as well as MoO$_2$ could be oxidized to MoO$_3$. Reaction as follows:

$$\text{Mo + O}_2 \rightarrow \text{MoO}_2$$
2MoO₂ + O₂ → 2MoO₃

Fig.3 revealed that it shaped sheet structure initially, and even better structure was formed in 600 °C (Fig.4).

Figure 5. SEM sample—anneal at 700°C for 2h, 10°C/min (a) upper surface -×500; (b) upper surface -×2000

Figure 6. EDS sample—anneal 600°C for 2h (Range unit: keV)

When we elevated temperature to 700 °C (Fig.5) , the integrity of the sheet structure was destroyed. Many experiments showed that ~600 °C were the optimum temperature to fabricate MoO₃ nanostructure materials. Layered structure was advantageous to the electronic movement and it was an ideal material for both redox and intercalation pseudocapacitance (Faraday pseudocapacitors as well).

Fig.6 EDS revealed that anneal could increase the percentage of Oxygen, and it was obvious that anneal made the reaction be easy between Molybdenum and Oxygen. We can obtain more pure MoO₃ nanostructure materials by increasing Oxygen gas percentage and lengthening annealing time.

X-ray Photoelectron Spectroscopy (XPS) was adopted to investigate the chemical state of Molybdenum and Oxygen after annealed at 600 °C (Fig.7a and Fig.7b respectively). As shown in Fig.6a, it was fitted with two peaks. Binding energy of the Mo 3d₅/₂ electron peak (232.90 eV,
reference with C1s) and another Mo 3d_{3/2} electron peak (236.00 eV, reference with C1s) in Fig.7a indicated a 6+ oxidation state identical with MoO_3.

![Figure 7. XPS sample (anneal 600°C for 2h)—Surface composition of nanosheet: (a) Mo3d peaks, (b) O1s peaks.](image)

The sample after etching and thermal treatment was cut into 1 cm * 0.5 cm and fixed wire, using silver paste and epoxy resin bonding molybdenum foil with wire on the back, and the whole molybdenum foils coated with epoxy resin on the back, playing a protective role. Putting it into DHG-9038A temperature drying oven and the temperature was set at 80 °C, time for 60 min. We cooled it down to room temperature.

Effects of MoO_3 capacitive capability was investigated by cyclic voltammetry technique in 0.5 M Na_2SO_4 solution. Silver-silver chloride electrode and platinum electrode were used as reference electrode and counter electrode respectively.

![Figure 8. Cyclic voltammetry curves of (a) sample A (500°C) and (b) sample B (600°C) after thermal treatment in 0.5 M Na_2SO_4 solution, Init E (V) = -1.15, High E (V) = 0.15 (a) / 0.3 (b), Low E (V) = -1.15, Init P/N = N, Segment = 40, Sample Interval (V) = 0.001, Quiet Time (sec) = 2, Sensitivity (A/V) = 0.01. Scan Rate (V/s) was 0.2, 0.15, 0.1, 0.05 and 0.01 respectively.](image)
In Fig. 8, the shapes of CV loops at scan rates from 10 mV / s to 200 mV / s were typically, which indicated the intrinsically pseudocapacitive properties of MoO$_3$. To some extent, the curves are not typically symmetric with a triangular shape, indicating severe polarization and slow charge transfer in the compact oxide film. Thermal treatment at 600 °C (sample B) shown better capacitor performance than 500 °C (sample A). Fig. 8a depicted five different scan rates CV curves of sample A. It can be easy to find that the less the scan rate was, the stable the curve be. When the scan rate was 10 mV / s, the electrode current was increasing gradually from -1.15 V ~ -1.10 V in the anode scanning process and -1.15 V ~ 0.15 V in the cathode scanning process, without obvious redox peaks. In this process, the reaction occurred between solution and electrode, H$^+$ adsorption and desorption.

The equivalent capacitance in the process of the electrode reaction could be calculated by formula (1):

$$ C = \frac{Q}{U} = \int idt \cdot \frac{du}{U} = \int idu \cdot \frac{du}{U} = \int idt \cdot \frac{du}{U} = \frac{Scv}{U \cdot v} \quad (1) $$

C: electrode capacitance; Q: electrode electric quantity; U: the window of CV scan; i: electrode current; v: scan rate; Scv: the CV curve integral area of the electrode current and the scan potential range.

We defined the electrode capacitance of anodized scan as $C_a$ and cathode scan as $C_c$, calculating $C_a$ and $C_c$ according formula (1). In terms of one sample electrode, the value of capacitance was decreasing when the scan rate improved. When $C_a$ was equal to $C_c$, we got the best capacitance performance ($\eta = \frac{C_a}{C_c}$).

<table>
<thead>
<tr>
<th>Scan rate (V/s)</th>
<th>Sample A (Thermal treatment after 500°C)</th>
<th>Sample B (Thermal treatment after 600°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$C_a$ (mF)</td>
<td>$C_c$ (mF)</td>
</tr>
<tr>
<td>0.01</td>
<td>123.85</td>
<td>129.23</td>
</tr>
<tr>
<td>0.05</td>
<td>57.85</td>
<td>58.30</td>
</tr>
<tr>
<td>0.1</td>
<td>39.77</td>
<td>39.77</td>
</tr>
<tr>
<td>0.15</td>
<td>33.13</td>
<td>33.84</td>
</tr>
<tr>
<td>0.2</td>
<td>29.58</td>
<td>31.69</td>
</tr>
</tbody>
</table>

Above of Table 1 data could be seen that sample A own better capacitance performance and much more stable than B. When the scan rate was 100 mV / s and 10 mV / s, sample A got the best reversible capacitance and largest capacitance respectively. When the scan rate was 50 mV / s and 10 mV / s, sample B got the best reversible capacitance and largest capacitance respectively. At the same time, the sample that was annealing on 700°C for 2 hours did not show any property of pseudocapacitor.
Table 2. Sample electrode electrochemical performance

<table>
<thead>
<tr>
<th>Sample</th>
<th>Q (C)</th>
<th>m (mg)</th>
<th>C_{ms} (F g^{-1})</th>
<th>\xi</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample A</td>
<td>0.329</td>
<td>4.4</td>
<td>28.76</td>
<td>0.0558</td>
</tr>
<tr>
<td>Sample B</td>
<td>0.343</td>
<td>4.6</td>
<td>30.85</td>
<td>0.0668</td>
</tr>
<tr>
<td>Sample C</td>
<td>-</td>
<td>5.0</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

In the solution of 0.5 M Na$_2$SO$_4$, scan rate as 10 mV / s, sample A, B and C electric quantity, the quantity of active substance and the quantity of specific capacitance was listed in Table 2.

\[ C_{ms} = \frac{C}{2m} \quad (2) \]

C_{ms}: the quantity of specific capacitance; C: the electrode capacitance of anodized scan; m: the quantity of MoO$_3$ in electrode.

The charge (Q, unit: C) that electrode stored can be calculate in the Cyclic Voltammetry tests, the formula was listed as (3).

\[ Q = \frac{S_v}{V} \quad (3) \]

In 0.5 M Na$_2$SO$_4$ solution, we set scan rate at 10 mV / s, some parameters such as electric quantity, the quantity of active substance and specific capacitance were displayed in Table 2. \( \xi \) represented the percentage of MoO$_3$ in redox reaction at electrode surface. It can be calculated by formula (4).

\[ \xi = \frac{C_{a}UM}{F} \quad (4) \]

C_{ms}: the quantity of specific capacitance; U: the window of CV scan; M: molar mass of MoO$_3$ (144 g mol$^{-1}$); F: the constant of Faraday (~96485.34 C mol$^{-1}$).

Table 2 described that sample B storage more charge than A as well as high percentage of MoO$_3$ in redox reaction at electrode surface. Therefore, the sample B performed best in three samples.

Fig.9a described A.C. impedance spectrum of sample B, frequency from 1 Hz to 100 KHz and voltage amplitude as 0.05 V. The curve had three regions, the high frequency area clearly showed the semicircle approximately and the electrode showed a half finite layer diffusion impedance behavior. When the frequency higher than 31.62 Hz, low initial zone became a straight line which slope was approximately equal to 1. In high frequency area, impedance curve and the real axis intersection point was 3.466 \( \Omega \), and high frequency half part of the impedance circle radius corresponding to the charge transfer impedance (Rct) was 3.703 \( \Omega \).

The double layer capacitance with high frequency half impedance dome point electrode electric (Cdl) can be calculated by formula (5), and C_{dl}=0.014 mF. Electrode got into half limited barrier layer transmission control process after 31.62 Hz.

\[ C_{dl} = \frac{1}{2\pi fR_{ct}} \quad (5) \]

Fig.9b described chronocoulometry (galvanostatic charge-discharge test) curves in 0.5 M Na$_2$SO$_4$ solution. We could conclude from red curve that the time of charge/discharge was equal, so
the redox reaction on sample electrode was quasi reversible. However, the potential would reduce when time increased.

$$C_{eq} = \frac{It}{mv}$$  \hspace{1cm} (6)

I: current density; t: pulse width; m: the quality of active substance; v: the window of voltage.

On the whole, the performance of capacitance was stable after 700 cycles, which capacitance consume was less than 13%. The specific capacitance was 30.66 F g$^{-1}$ that equal to the specific capacitance of CV.

A performance comparison of our work with other related supercapacitor is summarized in Table 3.

Figure 9. (a) A.C. Impedance Spectroscopy of sample B in 0.5 M Na$_2$SO$_4$ solution, Init E (V) = 0.05, High Frequency (Hz) = 1e+5, Low Frequency (Hz) = 1, Imp SF, Amplitude (V) = 0.005, Quiet Time (sec) = 2; (b) Chronocoulometry curves of sample B in 0.5 M Na$_2$SO$_4$ solution, Init E (V) = -0.3, Final E (V) = 0.3, Step = 8, Pulse Width (sec) = 0.25, Sample Interval (s) = 2.5e-4, Quiet Time (sec) = 2, Sensitivity (A/V) = 0.1

Table 3. Comparison of specific capacitance for supercapacitors

<table>
<thead>
<tr>
<th>Working electrode</th>
<th>Specific capacitance (F g$^{-1}$)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoO$_3$ nanostructure</td>
<td>30.85</td>
<td>This work</td>
</tr>
<tr>
<td>NiO/SiNW nanocomposite</td>
<td>681</td>
<td>[14]</td>
</tr>
<tr>
<td>NiO/silicon MCP</td>
<td>586.4</td>
<td>[15]</td>
</tr>
<tr>
<td>ZnO/C</td>
<td>21.7</td>
<td>[16]</td>
</tr>
<tr>
<td>Symmetric ZnO/carbon aerogel</td>
<td>25</td>
<td>[17]</td>
</tr>
<tr>
<td>Ni(OH)$_2$ / graphene sheets</td>
<td>1335</td>
<td>[18]</td>
</tr>
<tr>
<td>MnO$_2$ / graphene nanostructured</td>
<td>315</td>
<td>[19]</td>
</tr>
<tr>
<td>RuO$_2$ / graphene sheet</td>
<td>570</td>
<td>[20]</td>
</tr>
<tr>
<td>Single-walled carbon nanotube</td>
<td>180</td>
<td>[21]</td>
</tr>
<tr>
<td>Co$_3$O$_4$ nanosheet / Ni foam</td>
<td>1471</td>
<td>[22]</td>
</tr>
<tr>
<td>PEDOT-MoO$_3$</td>
<td>300</td>
<td>[23]</td>
</tr>
<tr>
<td>MoO$_3$</td>
<td>0.004</td>
<td>[23]</td>
</tr>
</tbody>
</table>
As is shown above, these results suggest that MoO$_3$ nanostructure increases from 40 mF g$^{-1}$ \[23\] to 30.85 F g$^{-1}$, which show that the MoO$_3$ nanostructure is a promising electrode material for supercapacitors. Compare with other 1D structure electrode like ZnO\[16\], MoO$_3$ prepared in this work have better specific capacitance performance. Mansoor Sarfraz’s work report that they obtain the MoO3 nanowires as an electrode, for electrochemical supercapacitors in water based electrolytes exhibits a specific capacitance of 36 F g$^{-1}$, but the same electrode in ethylammonium nitrate (EAN) electrolyte which is 8 times higher than the specific capacitance obtained from MoO3 nanowires in water based electrolyte[26]. Compare with this result, the specific capacitance performance is like us work, but the method we used is simplified, and it inspire we can change the other electrolyte to improve the specific capacitance performance. In this work we fabricate MoO$_3$ owns the superiority such as simple, low cost and easy to control the reaction process than other method, we can improve it capacitance performance by increase its dimension.

Recent reports demonstrate that 3D nanostructured materials such as porous frameworks, nanoparticles, nanowires and nanotubes can offer large a surface area, permanent porosity, high thermal stability, and significant enhancement of electrode performance. So the specific capacitance is will be higher when the electrode was synthesized into 3D structure. Table 1 demonstrate that 3D structure electrode have obvious advantage of capacitance, such as Co$_3$O$_4$ nanosheet/Ni foam[22], Ni(OH)$_2$/ graphene sheets[18], NiO/SiNW nanocomposite[14], PANI/MoO3/GNP[24], RuO$_2$/grapheme sheet[20], MnO$_2$/graphene nanostructured[19], NiO/silicon MCP[15], PEDOT-MoO$_3$[23] and PPy/MoO$_3$/GNR[25] exhibit specific capacitance of 1471 F g$^{-1}$, 1335 F g$^{-1}$, 681 F g$^{-1}$, 570 F g$^{-1}$, 593 F g$^{-1}$, 315 F g$^{-1}$, 586.4 F g$^{-1}$, 300 F g$^{-1}$ and 844 F g$^{-1}$ respectively.

These results from two indispensable factors, namely the high catalytic activity and the framework formed. Our next research direction is tried to combine molybdenum trioxide nanostructure materials with graphene sheets, to build the 3D framework. Considering the full utilization of the advantages of MoO$_3$ as electrochemical capacitors, we believe the novel electrodes can be applied in high-performance energy-storage systems.

<table>
<thead>
<tr>
<th>Electrode Combination</th>
<th>Capacity (F g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PANI/MoO$_3$/GNP</td>
<td>593 [24]</td>
</tr>
<tr>
<td>PPy/MoO$_3$/GNR</td>
<td>844 [25]</td>
</tr>
<tr>
<td>MoO$_3$ nanowires in EAN electrolyte</td>
<td>288 [26]</td>
</tr>
<tr>
<td>MoO$_3$ nanowires in water based electrolytes</td>
<td>36 [26]</td>
</tr>
</tbody>
</table>

4. CONCLUSIONS

Fabricating MoO$_3$ nanostructure materials in AgNO$_3$ / HNO$_3$ solution system is a novel method to MoO$_2$/ MoO$_3$ nanostructure materials, which is worthy to popularize. It’s easy to operate, friendly to environment, little to cost and AgNO$_3$ can be recycled. The specific capacitance is 30.85 F g$^{-1}$ at 10 mV / s in 0.5 M Na$_2$SO$_4$ solution, owning high performance of recycled with capacitance loss less than 13 %. A.C. impedance spectrum shows that double layer capacitance (C$_{dl}$) is 0.014 mF and electrode
gets into half limited barrier layer transmission control process after 31.62 Hz. Smaller as its specific capacitance is, the stable performance of CV and galvanostatic charge-discharge test suggests it can be ideal material for nano-composite materials (MoO$_3$ decorating with metal oxide such as TiO$_2$, SnO$_2$ and so on) electrochemical capacitor.

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