Full Paper

Facile Synthesis and Characterization of CeMoO₄ Nanostructure via Co-precipitation Method and Investigate its Application Supercapacitor

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Abstract- Here in, CeMoO₄ nanostructure were successfully prepared by a co-precipitation route without capping agent. The characterization and morphological of as-prepared samples were examined by Fourier transform infrared spectroscopy, filed emission scanning electron microscopy, X-ray diffraction, and energy dispersive X-ray spectroscopy. SEM and XRD results show that CeMoO₄ nanostructure obtained with average nano-plate thickness 30 nm and average crystal size of 10 nm. The evaluations on CeMoO₄-based electrodes revealed the material to have a specific capacitance (SC) of 327 F g⁻¹ at a scan rate of 2 mV s⁻¹, an energy density of 24.5 Wh kg⁻¹, and a high rate capability. Continues cyclic voltammetry evaluations using CeMoO₄-based electrodes proved the electrodes to be capable of maintaining almost 96.3% of its initial SC after 4000 cycles. To the best of our knowledge, this study is considered as the start point of using lanthanide molybdates as an electrode materials for supercapacitors and the results obviously consent to outstanding properties of CeMoO₄ for the mentioned application.

Keywords- CeMoO₄, Nanostructure, Co-precipitation, Supercapacitor
1. INTRODUCTION

Once dimension of materials become so small and turn into nanocrystalline materials their surface-to-volume ration in comparison with those of the bulk compounds considerably increase [1-8]. As a result, their optical, magnetic and electrical behaviors can drastically change, they are why such kinds of materials have been focused [9-20].

Of all rare-earth metals, cerium (Ce) constitutes largest quantity of such metals in the Earth's crust. Many rare earth based compounds like Ce or Er silicate, phosphate, tungstate, and vanadate minerals have been excavated, developed, and proceed to be tailored in industry and medicine. Structurally, cerium could be found in both tetravalent and trivalent states. Despite the fact that stability of the former arrangement is more than that of later one for covalent compounds, only a limited number of structures with Ce\(^{4+}\) ions have been well characterized. Structures with Ce(III) in the cation site appear more abundant, such as, Ce\(_2\)(MoO\(_4\))\(_3\) and CeO\(_2\) [21-23]. Molybdate structures with average catalytic activity have been well studied in literature [24,25]. For example, Le and coworkers [26], have reported the preparation and the selective oxidation of propylene through bismuth molybdate nanostructures (including \(\alpha\)-Bi\(_2\)Mo\(_3\)O\(_{12}\), \(\beta\)-Bi\(_2\)Mo\(_2\)O\(_9\), \(\gamma\)-Bi\(_2\)MoO\(_6\)). Cerium molybdenum oxides could be considered as an important family of structures, because they are being utilized as inorganic pigments in ceramics, paints, plastics [27], as well as in catalysis [28]. Therefore, the structure of oxides should be stable enough to provide color or act as catalysts for several cycles. Moreover, Cerium molybdate has been utilized as a corrosion inhibitive component to a non-chromate protective solution which are useful for coating of iron and iron alloys, particularly steel [29]. This work contains the synthesis of CeMoO\(_4\) nanostructure through the co-precipitation method. Supercapacitors are one of the energy storage devices that can save a lot of energy. They are used as an appropriate tool for exchanging electrical energy in areas where high power is required. Investigation of the capacitive behavior of synthesized electrode of CeMoO\(_4\) nanostructure was studied using various electrochemical techniques such as cyclic voltammetry and chronopotentiometry techniques.

2. EXPERIMENTAL

2.1. Characterization

\((\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot4\text{H}_2\text{O}, \text{and Ce(NO}_3\text{)}_3\cdot6\text{H}_2\text{O, were purchased from Aldrich Co. XRD pattern was performed by a Philips-X’PertPro. FESEM images were determined on LEO-1455VP. The EDS analysis was examined by XL30, Philips microscope. The FT-IR spectra were recorded on Magna-IR, spectrometer 550 Nicolet with 0.125 cm\(^{-1}\) resolution in KBr pellets in the range of 400-4000 cm\(^{-1}\).}$$
2.2. Synthesis of CeMoO$_4$ nanostructure

In a typical synthesis, in two separate beakers, (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O (1 mmol) and Ce(NO$_3$)$_3$·6H$_2$O (7 mmol) were dissolved in 40 mL of distilled water under stirring, separately, and then was mixed. The resulting solutions were vigorously stirred at 70 °C for 1 h and the obtained yellow precipitate was collected, dried at 100 °C, and finally was calcined at 500 °C for 60 min.

2.3 Electrochemical equipment

Cyclic voltammetry and electrochemical impedance spectroscopy techniques which was performed with PGSTAT204 equipped with a three-electrode system was used to study the electrochemical investigations. The same system was also used for charge-discharge tests. In the three-electrode system, Ag/AgCl and platinum rod were used as reference electrode and opposite electrode, respectively. In order to prepare the working electrode, a mixture of active material, graphite, carbon black and PTFE suspension were prepared with a 65: 20: 10: 5 mass ratio. A few drops of ethanol were added to the mixed components, and after drying the paste, a layer was pressed onto a 1 cm$^2$ stainless steel grid as a current collector and then it was placed at 80 °C for 4 h to dry completely. An aqueous solution of potassium chloride 3 M was used as electrolyte for electrochemical tests. Based on the cyclic voltammetry data, the SC of the materials used in the working electrodes can be obtained using the following equation:

$$SC = \frac{\int_i dV}{vmV}$$

In which $I$ represents current density (A), $V$ and $\nu$ are the potential (V) and its scan rate (V s$^{-1}$), and $m$ is the mass of the electroactive material (g).

3. RESULTS SECTION

3.1. Characterization

The XRD patterns of CeMoO$_4$ nanostructure have been displayed in Fig. 1. The spectrum of bare CeMoO$_4$ nanostructure shows a series of diffraction peaks at the place of 13.54° ((111) line), 28.04° ((221) line), 46.03° ((000) line), and 56.91° ((121) line) which is compatible with the standard JCPDS file of CeMoO$_4$ nanostructure cubic phase (JCPDS No. 00-030-0303). No other crystalline phases were observed in the calcined product. From XRD data, the crystallite diameter ($D_c$) of CeMoO$_4$ nanostructure after calcinations were found to be 17.6 nm through the Scherer equation [30-39]:

$$D_c = \frac{K\lambda}{\beta \cos \theta}$$
where $K$ is the shape factor, which is equal to 0.9. $\beta$ is the full width at half maximum of the corresponding diffraction peaks, and $\lambda$ is the wavelength of X-ray source used in XRD.

![XRD pattern](image1)

**Fig. 1.** XRD patterns of CeMoO$_4$ nanostructure prepared via co-precipitation route

The FESEM image revealed of CeMoO$_4$ nanostructure prepared by co-precipitation method. The production of CeMoO$_4$ nanostructure with a grain size covering between 20 to 40 nm was corroborated from SEM images as showed in Fig. 2. Fig. 3 indicates that the CeMoO$_4$ nanostructure were merely composed of Ce, Mo, and O.

![SEM image](image2)

**Fig. 2.** SEM images of CeMoO$_4$ nanostructure prepared via co-precipitation method
EDS analysis measurement results proved the CeMoO₄ nanostructure would be pure. For instance, Fig. 6 shows the FT-IR spectra of CeMoO₄ nanostructure synthesized by co-precipitation route. The characterization peaks in FT-IR are 594 cm⁻¹ (vibration of atoms: Ce–O at CeMoO₄ nanostructure) and 710 and 746 cm⁻¹ (vibration of atoms: O-Mo-O at CeMoO₄ nanostructure) [40].

3.2. Cyclic voltammetry

Fig. 5 shows a cyclic voltammogram of a CeMoO₄ nanostructure electrode in KCl (3M) electrolyte in the potential range of -0.9 to -0.1 at sweep rates of 5 to 200 mV s⁻¹. The rectangular shape of specie and I-E symmetry in various scan rates showing the very good reversibility of samples in the mentioned range. The electrochemical capacity of electrodes made of CeMoO₄ nanostructure is attributed to the oxidation and reduction of
oxy-cation present at the electrode surface. In aqueous solution, the switching between oxidation states of Ce(IV)/Ce(III) in CeMoO₄ nanostructure is possible. These transitions, which are accompanied with the proton or cation exchange with an electrolyte solution, obey from the following equation:

\[ \text{CeMoO}_4 + X^+ + e^- \rightarrow \text{CeMoO}_4X \]  

(3)

In which \( X^+ \) is proton or cation of the electrolyte, respectively. Fig. 5b shows the capacitance of cerium molybdate electrode at the various sweep rates (2-200 mV s\textsuperscript{-1}). The capacitance of a supercapacitor calculated for CeMoO₄ nanostructure at the scan rates of 2 mV s\textsuperscript{-1} is 327 F g\textsuperscript{-1}. As is evident in this diagram, the capacitance will be reduced with increase in the scan rate. This decrease in the capacitance of a supercapacitor is dependent on the morphology and diameter of the nanoparticle cavities. The decreasing amount of capacitance for CeMoO₄ nanostructure electrodes is 54%.

**Fig. 5.** (a) Voltammograms of the CeMoO₄ nanostructure at various sweep rates of (5-200 mV s\textsuperscript{-1}) in KCl (3 M); (b) SC vs. sweep rates for the CeMoO₄ nanostructure

### 3.3. Stability of Electrodes

The continuous cyclic voltammogram (CCV) technique was used for study of stability of the electrodes. This test was performed on the electrode with sweep rate of 250 mV s\textsuperscript{-1} in KCl electrolyte and specific capacitance of the samples was calculated during 4000 cycles of voltammetry. The corresponding specific capacitance of CeMoO₄ nanostructure electrodes is the 3.7 percentage of the initial value (Fig. 6). CeMoO₄ nanostructure electrode shows relatively poor performance and stability during consecutive voltammetry cycles, which can be related to the deactivation of active pores and sites on the surfaces of CeMoO₄ nanostructure. Figure 6b shows the 3D curves of continuous cyclic voltammogram for the electrode, which the variations in the voltammograms are seen well.
Fig. 6. (a) Cyclic performance of the CeMoO$_4$ nanostructure electrode at sweep rate of 250 mV s$^{-1}$, and (b) continuous cyclic voltammograms of the CeMoO$_4$ nanostructure measured at scan 250 mV s$^{-1}$

3.4. Charge/Discharge

In order to evaluate the performance of the electrode, a galvanostatic charge/discharge (GCD) technique (chronopotentiometry) is used. In this experiment, the CeMoO$_4$ nanostructure electrode was charged and discharged at different current densities (1 A g$^{-1}$ to 16 A g$^{-1}$). Figure 4-5 shows the chronopotentiogram of the above electrode in KCl electrolyte with a concentration of 0.3 M, which is obtained in the capacitive-voltage range (cyclic voltammetry potential range). Charge/discharge curves of the electrode show the linear variations in the potential in terms of current and symmetrical shape which is another characteristic of an ideal capacitor. Also, the ohmic drop in the electrode is very small and close to ideal. Figure 7 shows the capacitance of the CeMoO$_4$ nanostructure electrode at different current densities (1 A g$^{-1}$ to 16 A g$^{-1}$). The calculated supercapacitance of the CeMoO$_4$ nanostructure electrode in the current density 1 A g$^{-1}$ is 275 Fg$^{-1}$. As shown in the curve, capacitance increases with increasing the current densities. This decrease in supercapacitance is dependent on the morphology and diameter of the nanoparticle cavities. GCD data are in good agreement with the potentiostatic and cyclic voltammetry data and confirms these data. Ragone curves (power density in term of energy density) for CeMoO$_4$ nanostructure electrode are shown in Fig. 7. These curves are obtained from charge/discharge data at different current densities. The power density ($S_p$) and the energy density ($S_E$) of electrode are estimated using the following equation:

$$S_p = \frac{1 \times \Delta E}{2m}$$  \hspace{1cm} (4)

$$S_E = \frac{1 \times \Delta E \times \Delta t}{2m}$$  \hspace{1cm} (5)
where I, ΔE, ΔT and m represent the potential range, current, charge time and active substance content, respectively. CeMoO₄ nanostructure has power density of 400 W kg⁻¹ and energy density of 24 W h kg⁻¹. According to the obtained data, it can be noted to the high density of CeMoO₄ nanostructure which shows the good capacitance in low density powers. Considering the obtained curves, the energy density decreases by increasing the power density; the appropriate energy density at high power density is one of the main characteristics supercapacitive of the electrodes.

Fig. 7. (a) GCD curves of the CeMoO₄ electrode at various current densities (1 to 16 A g⁻¹); (b) SC vs. current density for the CeMoO₄ nanostructure electrode and (c) Ragone plots obtained for the CeMoO₄ nanostructure electrode

3.5. Electrochemical Impedance Spectroscopy

Figure 8 shows the Nyquist curves of CeMoO₄ nanostructure electrode in a KCl electrolyte at -0.45 V with frequency range of 0.01-10⁵ Hz. As seen in the figure, both curves are similar in appearance. The semicircle in the left-hand side, which is related to high frequencies implies the charge storage process at the contact of electrode surface with electrolyte. This semiconductor proceeds linearly with a slope of 45 to 90 degrees at intermediate frequencies, which is originated from the Warburg diffusion. In the low frequencies or in the right-hand side of the figure, the straight line is observed which indicates the capacitance behavior of the porous electrode. At high frequencies, the location of the collision with the horizontal curve is
called internal resistance or dissolution resistance, which is almost the same for all electrodes (same electrolytes). The diameter of the semicircle indicates the charge transfer resistance at the electrode surface which the lower value is indicator of ideal capacitive behavior.

![Impedance spectra of the CeMoO₄ electrode](image)

**Fig. 8.** Impedance spectra of the CeMoO₄ electrode, measured at an AC amplitude of 10 mV, in 3.0 M KCl aqueous electrolyte

4. CONCLUSION

In this study, the co-precipitation method for synthesizing CeMoO₄ nanostructure and examined by fourier transform infrared (FT-IR) spectroscopy, energy dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD), and filed emission scanning electron microscopy (FESEM). The study the capacitance behavior of the prepared cerium molybdate electrode showed that this electrode has a very good capacitive behavior. The rectangular shape of the capacitance of this electrode in cyclic voltammograms show this phenomenon. The specific capacitance of this electrode was 327 F g⁻¹. These results distinguished CeMoO₄ electrode as a potential candidate for application in electrochemical supercapacitors.

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