Ordered Mesoporous Carbon/MoO$_2$ Nanocomposites as Stable Supercapacitor Electrodes

Yuanyuan Zhou,a Chul Wee Lee,a Soo-Kil Kim,b,* and Songhun Yoon*a†

aGreen Chemical Technology Division, Korea Research Institute of Chemical Technology (KRICT) & University of Science and Technology (UST), Daejeon 305-600, Korea
bSchool of Integrative Engineering, Chung-Ang University, Heukseok-dong, Dongjak-gu, Seoul 156-756, Korea

Abstract

Novel ordered mesoporous carbon/MoO$_2$ nanocomposites were prepared using one-step tri-constituent co-assembly method. From various structural and physical analysis, ordered mesoporous structure with homogeneous dispersion of MoO$_2$ in nanoscale was observed in as-prepared composites containing from 9 to 38 wt% MoO$_2$, while gradual collapse of ordered structure appeared in higher MoO$_2$ fraction. When the prepared materials were applied into supercapacitor electrodes, the composite electrode with 33 wt% MoO$_2$ exhibited a high capacity from MoO$_2$ itself (395 F g$^{-1}$) and a very stable cycle performance of negligible capacity loss even after 500 cycles under strong acid electrolyte.

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With recent efforts to develop high-performance supercapacitor (SC) electrode materials, nanocomposites between metal oxides (e.g., MnO$_2$, MoO$_3$, CoO$_2$, VO$_2$, etc.) and ordered mesoporous carbon (OMC) have been intensively prepared by many researchers.1–4 These nanocomposite materials have exhibited improved capacitive performance due to the beneficial ordered mesoporous structure and the pseudocapacitive nature of the incorporated metal oxides.1–5 As a promising pseudocapacitive candidate, MoO$_3$, with forms of nanorod and nanocomposites with carbon nanotubes or conducting polymer, have been especially applied as SC electrodes.6–8 However, there exist several shortcomings such as complicated preparation, hazardous etching, low electrical conductivity and high solubility in strong acid electrolyte. In our previous research, an ordered mesoporous carbon–MoO$_3$ has been prepared by traditional post-addition method, which has shown an improved electrochemical performance. However, this preparative method requires further improvement due to its two-step complicated procedure and the relatively inhomogeneous result composite in its intrinsic structure. Especially, the still serious capacitance decay due to the fast dissolution of MoO$_2$ in the electrolyte retards its practical application, which should be attributed to the limited attachment between MoO$_2$ and carbon phase.

To overcome these obstacles, herein, triconstituent co-assembly method9 is introduced for the one-step preparation of the ordered mesoporous carbon–MoO$_2$ nanocomposites from a commercially available surfactant template (Pluronic F127) and a cheap Mo precursor (MoCl$_5$). Our products are therefore named as triconstituent ordered mesoporous carbon–MoO$_2$ nanocomposites (TMs). As MoCl$_5$ can be reacted with ethanol, the as-formed Mo=O bond can interact with hydroxyl groups (−OH) of resols through hydrogen bonding.9,10 Also, HCl product from the reaction can retard the MoO$_2$ precipitation even under a relatively humid environment, which indicates that our preparation can be repeated easily without control of humidity.10 Due to the strong interaction among carbon precursor, Mo precursor and F127, their evaporation-induced self-assembly (EISA) produces ordered mesostructure.9–12 After carbonization, TM materials are obtained. Initially, 0.5, 1, 2 and 3 mmol of MoCl$_5$ was reacted with 1 g of resol and 1.6 g of F127, and the corresponding samples were denoted as TM-0.5, TM-1, TM-2 and TM-3, respectively. Once they are prepared, their performances as SC electrode are investigated. To the best of our knowledge, this is the first report on the one-step synthesis of a completely ordered mesoporous nanocomposite between carbon and MoO$_2$. Also, due to the simultaneous formation of carbon phase and MoO$_2$ during the preparation process, it is expected that the as-formed MoO$_2$ are well confined in the carbon phase, which can possibly solve the active-material dissolution problem and thus enhance the cycleability.

*Electrochemical Society Active Member.
†Address correspondence to this author. E-mail: yoonsun@kRICT.re.kr

**Experimental**

Preparation of ordered mesoporous carbon/MoO$_2$ nanocomposites.—In a typical synthesis, 1.6 g of Pluronic F127 (Mw = 12,600 g mol$^{-1}$, PEO$_{106}$-PPO$_{70}$-PEO$_{106}$, BASF) was mixed with 8 g of ethanol at 40 °C under stirring until a clear solution (solution A) formed. 0.5 mmol of MoCl$_5$ was reacted with 5 g of ethanol to acquire a green solution (solution B). Solution B was added slowly into solution A under vigorous stirring. Sequentially, 5 g of 20 wt% resol ethanolic solution (prepared according to the references10,11,15) was added dropwise and then the color of the solution became darker. The result dark green solution was poured into several dishes and put in an ambient environment for about 24 hrs for full evaporation of the ethanol and HCl. The result gel-like green transparent film was heated at 100 °C for 24 h and a black soft film was acquired. After grinding, the film was calculated for 2 h at 450 °C and further at 600 °C in a N$_2$ atmosphere (the ramping rate is 2 °C min$^{-1}$ before 450 and 5 °C min$^{-1}$ after 600 °C). Finally, after cooling down to the room temperature, the product was collected and indexed as TM-0.5. TM-1, 2 and 3 material was prepared in the same procedure with adjusting the adding amount of MoCl$_5$ to 1, 2 and 3 mmol, respectively.

**Material characterization and supercapacitive performance investigation.—**The N$_2$ sorption isotherms were obtain on Micromeritics ASAP 2010 work-station and pore size distributions (PSD) were calculated by the Brunauer-Emmitt-Teller method.

The material morphology was scanned by a transmission electron microscope (TEM, JEOL JEM-2010). The energy dispersive X-ray analysis was conducted using the EDX analyzer equipped with the TEM in point mode and area mode. The X-ray diffraction (XRD) patterns were obtained with a Rigaku D/Max-SC diffractometer equipped with a rotating anode and Cu K$_\alpha$ radiation (λ = 0.15418 nm). A aluminum substrate was used for the small-angle XRD (2θ = 0.6°–3°) while a glass substrate was used for the wide-angle XRD (2θ = 5°–80°). X-ray photoelectron spectroscopy (XPS) experiment was carried out in a ultrahigh vacuum using the Scienta ESCA-300 high-resolution X-ray photoelectron spectrometer. The Mo elemental fraction was determined using Agilent 7700× inductively coupled plasma (ICP) mass spectrometry.

To prepare a supercapacitor electrode, a mixture of prepared TM materials and polytetrafluoroethylene (PTFE) binder, carbon black (10:1:1 in weight ratio) was dispersed in isopropanol and coated on a round Ti net of 1 cm$^2$ as the current collector. The electrode resistance was negligible when 10 wt% conducting materials were added. The resulting electrode plate was pressed and dried under vacuum at 120 °C for 12 hrs. Here, Pt flag counter and SCE reference electrodes were used for three-electrode cell system using 1.0 M H$_2$SO$_4$ electrolyte. Cyclic voltammetry (CV) testing was conducted with a voltage range from −0.2 to −0.6 V vs SCE on the Iviun.
potentiostat and the scan rate was varied from 2 to 20 mV s\(^{-1}\). Galvanostatic charge-discharge testing was carried out using WBCS-3000 battery cycler (Xeno Co.). The capacitance is calculated using the equation of \(C = \frac{Q}{\Delta U \Delta t}\). Herein, \(S\) is the integration area of cyclic voltammogram, \(m\) is the loading mass of the active material, \(k\) is the scan rate, \(U\) is the voltage gap during the cyclic voltammetry.

**Results and Discussion**

**Characterization of TM materials.**—Fig. 1 displays the charge-storage mechanism of TM materials as supercapacitor electrodes. As shown, it is expected that ordered mesoporous carbon matrix not only plays a role of highly electrical conductive skeleton, but also facilitates the electrolyte penetration through the mesopores. Pseudocapacitive faradaic reactions occur on embedded nanosized MoO\(_2\) while the electric double-layer forms on the porous carbon surface. Hence, both MoO\(_2\) and carbon surface, which are exposed to the acid electrolyte, can be contributive in capacitive charge-storage. Fig. 2 exhibited the small-angle and wide-angle X-ray diffraction (XRD) patterns. From the former patterns, a highly ordered structure with hexagonally pore packing (a space group of \(p6mm\)) was observed in TM-0.5 while the peak intensity became weaker with an increase of MoO\(_2\) fraction, indicative of a gradual collapse of the ordered mesostructure. Lattice parameter of 9 nm remained invariant, which were calculated from the (100) peak at 2\(\theta\) = 1.0°. From the latter patterns, furthermore, weak peaks associated with MoO\(_2\) (JCPDS PDF #32-0671) could be observed until TM-2, but clear MoO\(_2\) peaks appeared in TM-3, implying higher MoO\(_2\) crystallinity.

Fig. 3a–3d show the TEM images of TM-0.5, –1, –2 and –3 materials, respectively. As can be seen, highly ordered mesopores appeared in TM-0.5 whereas nanosized MoO\(_2\) crystals with high contrast to the amorphous carbon pore walls became more populated as MoO\(_2\) fraction increased. Our preliminary experiments using the point and area mode in the elemental analysis indicated that carbon, molybdenum and oxygen were all homogeneously dispersed within the ordered structures in TM-0.5 (not-shown here). From ICP analysis, The MoO\(_2\) fraction of TM-0.5, TM-1, TM-2 and TM-3 is 9 wt%, 17 wt%, 29 wt% and 38 wt%, respectively. With an increase of MoO\(_2\) fraction, the ordered mesoporous structure was gradually converted into wormhole-like structure, which coincided to the small-angle XRD results. Also, from the images, identical pore size of around 3–4 nm was estimated for all TM materials. In Fig. 3e, N\(_2\) sorption isotherms for TMs are shown, from which, the adsorbed N\(_2\) volume became smaller as MoO\(_2\) mole increased. From the change of pore size distributions (PSDs), shown in Fig. 3f, a monodispersed PSD was observed for TM-0.5 materials with a diameter of 3.4 nm, which is in good agreement with the estimated value from the TEM images and similar to soft-templated OMCs with F127 as the structure-directing agent in the literatures. However, the PSD became gradually more board and dispersed in higher MoO\(_2\) concentration cases, although similar pore sizes were observed. This reflected that a structural collapse happened when more Mo precursors were added, which was in good agreement with the XRD and TEM analysis. This indicated that a large amount of MoO\(_2\) gave rise to a decrease of interaction between resol and surfactant. And meanwhile measured BET surface areas were decreased from 640 to 381 m\(^2\) g\(^{-1}\) according to increase of MoO\(_2\), which should be ascribed from the negative co-effect of the density increase, the pore structure collapse and the MoO\(_2\) crystallinity increase.

**Supercapacitor performance of prepared materials.**—In Fig. 4, electrochemical performance of TM materials as supercapacitor electrodes is shown. Similar to the literature, the capacitance of pure OMC (MC) electrode prepared without a molybdenum precursor was very low, which was probably related to the poor connectivity and detrimental functional groups on the carbon surface due to a relatively low carbonization temperature of 600°C. Similarly, very low capacitance was observed for TM-0.5 and TM-1. As MoO\(_2\) increased, however, capacitance became larger and high increase of capacitance was observed in TM-2 and TM-3 electrode. This reflected that...
the capacitance in TM electrodes was dominantly originated from pseudocapacitive reaction in MoO$_2$ surface while capacitive contribution by electric double layer charging at carbon surface was negligible. Also, an abrupt rise of capacitance in TM-3 electrode implies that MoO$_2$ became well exposed to electrolyte, while electrolyte was hard to access to MoO$_2$ surface in other TM electrodes due to its complete inclusion by carbon wall. All these above implied that TM-3 material was the most suitable candidate as a supercapacitor electrode although it had a relatively low surface area and partially collapsed ordered structure. Hence, TM-3 electrode is selected for further discussion. The average capacitance of TM-3 electrode ($C$) was around 150 F g$^{-1}$ and thus the average capacitance of MoO$_2$ itself ($C_{MoO_2}$) considering its fraction of 38% ($x_{MoO_2}$) in the composite, was calculated as high as 395 F g$^{-1}$ ($C_{MoO_2} = C / x_{MoO_2}$), which is comparable to the highest value ever reported. While the characteristic three peaks were observed in electrode material prepared by post-addition of Mo precursor into OMC, broad two or three peaks were observed in our TM electrodes, which can be due to the low crystallinity of the nanosized MoO$_2$ crystals. Fig. 4b shows change of specific capacitance of TM-3 electrode according to increase of scan rate, which exhibited a gradual shape collapse. This scan rate dependency of TM-3 is reasonable when considering its pseudocapactive charge-storage feature, which is relatively slower than EDLC. While the two capacities became similar at 0.5 A cm$^{-2}$ current rate, indicating that additional slow reactions happened at low current rate during reduction process. This result requires further investigation. Fig. 4d shows cycle performance of TM-3 electrode until 500 cycles. Capacity remained invariant even after 500 cycles. Capacity retention of 80 ~ 90% after 50 cycles has been reported for MoO$_2$ nanorod or OMC/MoO$_2$ prepared by post-addition method, attributed to partial dissolution of MoO$_2$ under strong acid electrolyte (1 M H$_2$SO$_4$). To our best knowledge, our TM-3 electrode showed the most stable cycle performance in the strong acidic electrolyte environment. This remarkable advance in cycle performance should be benefited from the formation of complete nanocomposite between MoO$_2$ and carbon with their strong molecular interaction.

Conclusion

In conclusion, the ordered mesoporous carbon-MoO$_2$ nanocomposites were prepared by a simple triconstituent co-assembly method. As the embedded MoO$_2$ in the composites does a dominant contribution to the total capacitive performance, the prepared composite with the highest MoO$_2$ fraction exhibits the highest capacitance in spite of a partial collapse of ordered structure and a decrease of surface area. Also, due to the strong attachment between MoO$_2$ and carbon skeleton, extremely stable cycle performance were observed for our composite, which processes the potential use of our composite materials in the practical application.

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