Fabrication of CuO/C films with sisal-like hierarchical microstructures and its application in lithium ion batteries

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1. Introduction

Recently, transition metal oxides MO (such as CuO, NiO, CoO, etc.) were investigated as novel anode materials for lithium ion batteries due to their high theoretical capacities and good safety [1,2]. Much effort had been devoted to the synthesis of MO with various morphologies and dimensions. Some examples of these methods included electrochemical synthesis [3], thermal decomposition [4], spray pyrolysis [5], thermal oxidation [6,7], solution immersion [8,9], hydrothermal synthesis [10], template synthesis [11,12] and so on. It is now well established that morphology and crystallinity are important factors that affect the electrochemical properties of MO [13–15].

However, there are two shortcomings limiting the application of MO in lithium ion batteries. At first, transition metal oxides are poor semiconductors and the low electronic conductivities of MO particles restrict charge transfer process. Though adding conductive agents (e.g. carbon black) will improve the electrical contact between MO particles, forming a well-dispersed conducting network within active materials is still a challenge. Second, the cyclabilities of MO electrodes are significantly affected by volume change of MO particles. In course of lithium insertion-extraction, MO particles will pulverize into smaller particles, leading to the electrical isolation of electrodes. An effective solution to this problem is to prepare nanoscale MO [16,17]. Nevertheless, the aggregation of nanomaterials during cycling process will compromise the virtues of nanostructures.

To alleviate the volume changes and improve the conductivities of MO electrodes, forming composites with carbon was an effective method [18–20]. Recently, it was also proven that binary hierarchical structures at micrometer and nanometer scales were beneficial to the mechanical stability of nanostructures [21] and this concept had been widely used to construct superhydrophobic surfaces [22,23]. To our knowledge, however, little attention was paid to the fabrication of film-electrode with hierarchical structures for lithium ion batteries [24].

To combine the advantages of composite materials and hierarchical structures, we fabricate novel CuO/C composite films with sisal-like micro/nanometer binary structures. The goal is achieved by immersing copper plates in an ethanol solution of 4-aminobenzoic acid and subsequent heat treatment at 260 °C. X-ray diffraction, scanning electron microscope, galvanostatic discharge-charge measurement and cyclic voltammetry were employed to characterize the structures and electrochemical performance of the composite films. The CuO/C films exhibited reversible capacities greater than 600 mAh g⁻¹, good cyclability, as well as high rate capability as negative electrodes of lithium ion batteries. It was believed that the advantages of composites materials and binary hierarchical structures were responsible for the excellent electrochemical performance.

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Fig. 1. SEM images of the copper plates immersed in 30 mM ethanol solution of 4-aminobenzoic acid for (a) 24 h, (b) 72 h, (c) 96 h and (d) is the enlarged view of a sisal-like cluster.

Fig. 2. (a) TGA traces of a Cu(COOC₆H₄NH₂)₂ film obtained at 10 °C min⁻¹ under argon flux; (b) XRD plot of the resulting CuO/C film. Immersion time: 4 days.
molecules. We demonstrate here that the CuO/C films show excellent electrochemical performance as negative electrodes in lithium ion batteries.

2. Experimental

The fabrication of CuO/C films with sisal-like microstructures was carried out as follows. At first, copper plates (2 cm × 2 cm) were successively washed with ethanol and acetone to remove surface impurities. Then the copper plates were immersed in an ethanol solution containing 30 mM 4-aminobenzoic acid (PABA) at room temperature for different duration time. After being rinsed with ethanol, the resulting copper plates were heated at 260 °C for half an hour in a quartz-tube under argon atmosphere.

The obtained CuO/C films were cut into 1 cm² circle plates and used as the working electrodes. Lithium foils were used as the counter and the reference electrodes. The electrolyte solution was 1.0 M LiPF₆ in EC/DMC (1:1 by volume). Coin cells were assembled in a glove-box filled with argon. The electrochemical performance of the cells was evaluated by galvanostatic discharge–charge measurement using a computer-controlled battery tester. Cyclic voltammograms (CVs) were recorded on a CHI604 potentiostat at a scan rate of 1.0 mV s⁻¹. All the potentials indicated here were referenced to the Li/Li⁺ electrode potential.

The mass of active CuO/C on copper plates was estimated to about 4.0 mg cm⁻² according to the procedure described in Ref. [17].

X-ray photoelectron spectroscopy (XPS; PHI 5700 ESCA SYSTEM) was performed in an ultrahigh vacuum (UHV, 2.5 × 10⁻¹⁰ Torr base pressure) with the use of a monochromatic Al Kα source (1486.6 eV). FT-IR spectra were recorded on a PerkinElmer 98 apparatus (FT-IR Spectrometer 1000). X-ray diffraction (XRD) analysis was carried out by using Philips PW-1830. Thermogravimetric analysis (TGA) was performed on a NETZSCH TG 209 in an argon flow and at a heating rate of 10 °C min⁻¹. Scanning electron microscopy (SEM) images and energy dispersive X-ray microanalysis (EDAX) patterns were obtained with a JEOL JSM-6700F scanning electron microscope.

3. Results and discussion

The surface morphologies of the copper plates immersed in an ethanol solution of 4-aminobenzoic acid were investigated by SEM, as shown in Fig. 1. It is observed that the copper surfaces are covered by sisal-like clusters. The clusters are built from nanosheets of a few micrometers in length, 0.5–1.0 μm in width, and hundreds nanometers in thickness, indicating the presence of binary geometric structures at both micro and nanometer scales. The time-dependence of the surface morphologies was also illustrated in Fig. 1. Only a few sisal-like clusters distribute on copper surface at the initial immersion stage. Then more and more clusters cover the surface, and these clusters coalesce into a compact film as the immersion time closes to 96 h.
Fig. 4. SEM images of a CuO/C composite film at different magnifications. Immersion time: 4 days.

Fig. 5. Cyclic voltammograms (a) and discharge–charge profiles (b) of a CuO/C electrode. Immersion time: 4 days.
XPS and FT-IR were employed to identify the chemical compositions of the sisal-like clusters (see supporting information). These measurements confirm that the sisal-like clusters are mainly Cu(COOC$_6$H$_4$NH$_2$)$_2$ compounds, indicating hierarchical assembly of organic molecules on the copper surfaces [32,33]. On the basis of above results, we conclude that the sisal-like Cu(COOC$_6$H$_4$NH$_2$)$_2$ clusters with nano/microstructures can be constructed on copper surfaces by immersing copper plates in an ethanol solution of 4-aminobenzoic acid.

The conversion of Cu(COOC$_6$H$_4$NH$_2$)$_2$ films into CuO/C composite films was firstly studied by thermogravimetric analysis, as illustrated in Fig. 2a. The Cu(COOC$_6$H$_4$NH$_2$)$_2$ film loses about 0.5% of its weight at temperature lower than 100 °C. This weight loss is most likely associated with the release of the adsorbed water on the film surface. Then an abrupt weight loss (about 3.4%) occurs in the temperature range of 250–300 °C. This process is believed to result from the decomposition of Cu(COOC$_6$H$_4$NH$_2$)$_2$ into CuO and carbon. Based on the TGA result, we prepared CuO/C composite films at 260 °C. After heat treatment, the composition of the resulting films was identified by XRD, as shown in Fig. 2b. According to the JCPDS file (card no. 45–0937), the peaks can be ascribed to monoclinic-phase CuO. In the XRD pattern, almost no peak of carbon can be observed, indicating that the carbon is amorphous.

Fig. 3a and b shows the TEM images of a CuO/C film. The images display that the nanosheet is about 100 nm in width and few micrometers in length. It is clear that there is a distinct contrast difference in the image, suggesting the existence of two phases, amorphous carbon and CuO particles. The nanosheet is built from uniformly distributed CuO particles of 10–20 nm in diameter. The distance between CuO particles is about 20 nm. As shown in Fig. 3a, the CuO particles are homogeneously separated by amorphous carbon and there is no space left. Further EDAX confirms the presence of carbon, as shown in Fig. 3c. The content of carbon in the composite film is about 10.1 wt%.

Fig. 4 shows the SEM images of a CuO/C film. On the whole, the film exhibits similar sisal-like morphologies as those in Fig. 1, indicating that the heat treatment does not exert a significant impact on the final morphologies of the as-prepared film (though some collapse occur after heat treatment). The above results demonstrate that the CuO/C films with sisal-like hierarchical microstructures can be fabricated on copper plates via simple solution immersion and subsequent heat treatment.

The electrochemical performance of the CuO/C films in lithium ion batteries was evaluated by cyclic voltammetry and galvanostatic discharge–charge measurement. Fig. 5a shows the cyclic voltammograms of a CuO/C electrode between 0 V and 3.0 V at a scan rate of 1.0 m s$^{-1}$. In the first scan, there are three cathodic peaks located at 1.75 V, 0.71 V and 0.51 V, which can be attributed to a multi-step electrochemical reaction including (i) the creation of a CuI$_{1-x}$O$_x$(0 ≤ x ≤ 0.4) solid solution with a CuO phase, (ii) the formation of Cu$_2$O phase, and (iii) the conversion of Cu$_2$O into Cu and Li$_2$O [14,34]. In contrast, only two anodic peaks are observed at 2.54 V and 2.77 V. The strong peak at 2.54 V is related to the partial oxidation of Cu$_2$O into Cu$_2$O$_x$ and CuO [14,35]. After the initial scan, the cathodic peaks exhibit anodic shift and their intensities decrease significantly, implying the presence of the irreversible capacity loss.

Fig. 5b displays the first two discharge–charge profiles of a CuO/C electrode at a current density of 0.10 mA cm$^{-2}$. The voltage profiles are similar to those reported for powder form CuO [34,36,37]. The plateaus on the voltage profiles are consistent with the CV peaks in Fig. 5a. The initial discharge capacity of this CuO/C electrode is about 1084 mAh g$^{-1}$, while its charge capacity closes to 502 mAh g$^{-1}$. The extra discharge capacity of the electrode is due to the formation of a SEI-like (solid electrolyte interface) organic layer on the surfaces of copper particles [38]. It is believed that the sisal-like clusters will provide a large surface area to form such an organic layer.

The cycling performance of the CuO/C electrodes was tested at various current densities, and the results are shown in Fig. 6. For comparison, the data of a flower-like CuO film were also included [30], as illustrated in Table 1. The CuO/C electrode keeps a discharge capacity over 660 mAh g$^{-1}$ even after 50th cycle, while the flower-like CuO electrode only delivers a capacity of 547 mAh g$^{-1}$, indicating better cyclability of the CuO/C electrode. It should be noted that an increase in capacity upon cycling process is observed for the CuO/C electrode, which is a typical characteristic of the nanostructured transition metal oxides [39]. The CuO/C electrodes

### Table 1
Comparison on the electrochemical performance of CuO/C and CuO electrodes.

<table>
<thead>
<tr>
<th>Cycle Type</th>
<th>Sisal-like CuO/C (mAh g$^{-1}$)</th>
<th>Flower-like CuO (mAh g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10th cycle</td>
<td>630</td>
<td>607</td>
</tr>
<tr>
<td>20th cycle</td>
<td>664</td>
<td>589</td>
</tr>
<tr>
<td>30th cycle</td>
<td>663</td>
<td>569</td>
</tr>
<tr>
<td>40th cycle</td>
<td>664</td>
<td>554</td>
</tr>
<tr>
<td>50th cycle</td>
<td>664</td>
<td>547</td>
</tr>
<tr>
<td>0.5 C</td>
<td>671</td>
<td>552</td>
</tr>
<tr>
<td>1.2 C</td>
<td>532</td>
<td>476</td>
</tr>
<tr>
<td>2.0 C</td>
<td>447</td>
<td>391</td>
</tr>
<tr>
<td>4.0 C</td>
<td>435</td>
<td>341</td>
</tr>
</tbody>
</table>
also show better rate capability than those flower-like CuO counterparts, and the discharge capacities as a function of rates are plotted in Fig. 6b. It is observed that the CuO/C electrodes exhibits capacities of 660 mAh g\(^{-1}\) at 0.2 C (1 C = 670 mAh g\(^{-1}\)), but they are able to keep capacities around 410 mAh g\(^{-1}\) even at 4.0 C. On the contrary, the CuO electrode only shows a value of 341 mAh g\(^{-1}\) at 4.0 C. Therefore, these novel CuO/C films are promising negative electrodes for lithium ion batteries, which have the characteristics of high reversible capacity, good cyclability, and high rate capability.

The excellent electrochemical performance of the CuO/C electrodes may originate from the unique sisal-like hierarchical morphologies and the well-dispersed carbon. At first, the nanosheets of sisal-like clusters offer large electrode/electrolyte contact area and short diffusion path for lithium ions and electrons, which is favorable for the fast transportation of lithium ions and electrons within CuO particles at high rate; while the binary structure clusters guarantee the mechanical stability of the nanosheets [21]. Second, the homogeneously dispersed carbon acts not only as a barrier to suppress the aggregation and pulverization of CuO particles, but also as a buffering matrix to relax the expansion of CuO particles upon lithiation/delithiation process [19,20,40–44]. In addition, the carbon enhances the electrical contact between CuO particles [45,46] and favors the electrode kinetics at electrode/electrolyte interface to take place. In a word, the CuO/C electrodes combine the advantages of hierarchical structures and composite materials, and therefore possessing larger reversible capacity, better cyclability and higher rate capability than those CuO electrodes.

4. Conclusions

In summary, we fabricate novel CuO/C films with sisal-like microstructures by means of solution immersion and subsequent heat treatment. The resulting films exhibit reversible capacity greater than 600 mAh g\(^{-1}\), good cyclability, as well as high rate capability as negative electrodes in lithium ion batteries. The excellent electrochemical performance of the CuO/C films is believed to result from the unique hierarchical structures of the sisal-like clusters and homogeneously dispersed carbon. The results of this study demonstrate that preparing composite films with hierarchical morphologies is an effective way to improve the electrochemical performance of film-electrode in lithium ion batteries.

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Appendix A. Supplementary data


References