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Facile hydrothermal synthesis of CuFeO₂ hexagonal platelets/rings and graphene composites as anode material for lithium ion batteries

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Delafossite CuFeO₂ hexagonal platelets/rings and graphene composites were synthesized by a low temperature hydrothermal method. The formation mechanism of CuFeO₂ hexagonal platelets/rings follows the combined effects of both GO and NaOH. The obtained composites as anode material display a good battery performance with high reversible capacity, good rete capability and cyclic stability.

In recent years, lithium ion batteries (LIBs) have become the dominating power sources for portable electronics due to their high energy density and long cycle lifespan. Recently, the application for LIBs is expanding to a large scale, particularly electrical/hybrid vehicles and grid storage. However, graphite as the conventional anode material for LIBs cannot satisfy the increasing demands due to its low theoretical capacity (372 mAh g⁻¹). Therefore, seeking alternative anode materials with a better electrochemical performance has become an instant task. Ternary transition metal oxides, such as CuFeO₂, CuCo₂O₄, and ZnFe₂O₄, have been widely studied as very appealing anode materials to replace graphite due to their high theoretical capacity. Compared with them, CuFeO₂, the first known delafossite structure compound possesses stable compositions in the Cu-Fe-O ternary system, has seldom been investigated as anode materials for LIBs. The delafossite structure is constructed from alternate layers of two-dimensional close-packed copper cations with linear O-Cu-O bonds and slightly distorted edge-shared FeO₄ octahedra, and each oxygen is coordinated by four cations (one Cu⁺ and three Fe³⁺). Most of the synthesis methods of CuFeO₂ involve high temperature process, such as high temperature solid state reactions, sol-gel method with an after-treatment at high temperature, or high temperature hydrothermal method. The delafossite CuFeO₂ has attracted much attention due to its unique crystal structures and potential applications in catalyst, p-type conducting oxide, and antimicrobial material. Recently, Qiu et al. developed a low temperature hydrothermal method to prepare CuFeO₂ crystals as an antimicrobial material. The feasibility of CuFeO₂ crystals as anode material has been proved by Liu’s group in 2011. However, the particles aggregation occurs during the cycling process and low conductivity lead to fast capacity fade and poor cycling performance, which limit its application in LIBs.

Graphene is widely used to prepare various hybrid materials due to its unique electrical, mechanical, and surface properties. Graphene-based transition metal oxide composites have been widely reported in LIBs, due to the synergy effects between graphene and transition metal oxides. The functional groups attached on graphene oxide (GO) sheets play an important role in nucleation and growth of nanomaterials. Recently, Bando et al. reported that the acidic functional groups (-OH and -COOH) on GO can be used as etchants to fabricate a layered metal oxide nanoring-graphene hybrid. The nanoring on graphene would increase surface area and short Li⁺ ions transport length that lead to high electrochemical performance.

Here, we present a facile, one-pot, and low temperature (180 °C) hydrothermal method to prepare delafossite CuFeO₂ hexagonal platelets/rings and graphene (CuFeO₂/G) composites by using propionaldehyde as a reducing agent (see ESI for experimental details). The electrochemical performance of CuFeO₂/G composites as anode material in LIBs was investigated. Compared with CuFeO₂ crystals, the as-prepared CuFeO₂/G composites exhibit better electrochemical performances, such as high specific capacity, good rate capability and cyclic stability.

The typical XRD pattern of CuFeO₂/G composites, Fig. 1(a), shows that all of the diffraction peaks and relative intensities are consistent with standard crystallographic data (Delafossite, PDF, 00-012-0752) which confirm the good crystallinity of the CuFeO₂ phase. The CuFeO₂/G composites crystallize in a rhombohedral structure and belong to the space group R-3m with a=3.031 Å, c=17.140 Å. An unambiguous diffraction hump appearing in the range of ~24-28° was ascribed to the stacking of graphene sheets. The structural change of the carbon network occurring during the chemical processing form GO to graphene were characterized by Raman spectroscopy. Raman spectra of GO and CuFeO₂/G composites are shown in Fig. 1(b). The Raman spectrum of GO has typical G and D bands located at 1592 and 1349 cm⁻¹, respectively. A general characteristic of the reduction of GO is that the G band shifts to lower wavenumber. Raman spectrum of CuFeO₂/G composites...
also possesses G and D bands, while the G band shifts to 1588 cm$^{-1}$ suggesting the reduction of GO. The second benchmark of the reduction of GO is increase in peak intensity ratio between D and G bands ($I_D/I_G$). The $I_D/I_G$ ratio for CuFeO$_2$/G composites was calculated to be ~1.33 which is higher than that of GO (~0.84), further confirming the reduction of GO. The presence of a peak at 2667 cm$^{-1}$ which also shows a substantial increase in the disorder present the representative morphology of CuFeO$_2$ composites was calculated to be ~1.33 which is higher than that of GO (~0.84), further confirming the reduction of GO. The presence of a peak at 2667 cm$^{-1}$ which also shows a substantial increase in the disorder.

The morphology and microstructure of CuFeO$_2$/G composites were characterized by SEM, TEM, and HRTEM. The typical SEM image of pure CuFeO$_2$ crystals with well-defined edges, corners, and smooth surfaces of rhombohedral structure in overall size of ~0.8-2.5 µm is shown in Fig. 2(a). The lattice spacing of 0.224 and 0.284 nm are in good agreement with the (104) and (006) planes of the delafossite CuFeO$_2$. The result demonstrates the well-textured and single-crystalline nature of CuFeO$_2$ in the composites.

In order to demonstrate the feasibility of CuFeO$_2$/G composites as anode material for LIBs, we conducted investigations on their electrochemical performance. The CV analysis was applied to present the electrochemical details at a scan rate of 0.1 mV s$^{-1}$ within a voltage window of 0.005-3 V (vs. Li$^+$/Li$^-$). As shown in Fig. 3(a), the broad peak at ~0.73 V with an onset at ~1.15 V for the first cathodic cycle should be assigned to the reduction process CuFeO$_2$ + 4Li$^+$ + 4 e$^-$$ \rightarrow$ Cu$^0$ + Fe$^0$ + 2Li$_2$O, 2C + Li$^+$ + e$^-$$ \rightarrow$ LiC, and the irreversible reaction related to the decomposition of the electrolyte. The first broad anodic peak appeared at ~1.68 V should be attributed to the oxidation of both the Cu$^0$ and Fe$^0$ to CuO and Fe$_2$O$_3$, respectively. After the first cycle, both cathodic and anodic peaks shift to the higher voltage ranges and the current decreases revealing the existence of certain degree of irreversibility of the redox reaction. In addition, the CV curves almost overlap after the first cycle, suggesting the insertion/extraction of lithium ions taking place to the same extent. The similar characteristics were also performed in the galvanostatic charge/discharge voltage profiles of CuFeO$_2$/G composites at a current density of 100 mA$^{-1}$ between 0.005 and 3 V (Fig. S3, see ESI for details).

The rate capability (Fig. 3(b)) of CuFeO$_2$/G composites was tested at various current rates from 0.1 C to 2 C for 10 cycles at each current rate (1 C=708 mAh g$^{-1}$). It can be found that the capacities decrease as cycling current rates increase, which is caused by the low diffusion rate of the Li$^+$ ions into anode at high rates. The first discharge and charge capacities of CuFeO$_2$/G composites are 1571 and 944 mAh g$^{-1}$ higher than the theoretical capacity of bulk CuFeO$_2$ (708 mAh g$^{-1}$), which are attributed to the formation of a pseudo-capacitive gel-like film. The initial capacity loss may result from the incomplete conversion reaction and irreversible lithium loss caused by the formation of a solid electrolyte interphase (SEI) layer. When the current rate was brought down to 0.2 C after 50 cycles, a stable highly reversible capacity of 607 mAh g$^{-1}$ could be recovered. To further evaluate the cyclic stability, new cells were assembled and cycled at 0.2 C as illustrated in Fig. 3(c). For the CuFeO$_2$ crystals, the reversible capacity gradually dropped to ~117 mAh g$^{-1}$ after 100 cycles. The poor cycling performance of CuFeO$_2$ crystals could result from the inherent poor electronic and ionic conductivity. In contrast to CuFeO$_2$/G composites, the reversible capacity decreased to ~640 mAh g$^{-1}$ after 50 cycles, and then steadily increased to ~670 mAh g$^{-1}$ after 100 cycles. The reversible capacity was maintained at ~440 mAh g$^{-1}$ after 100 cycles tested at 1C as in Fig. S4 (see ESI for details). The capacity rises after prolonged cycling is a widespread phenomenon for transition metal.

![Fig. 1](image1.png) (a) XRD pattern of CuFeO$_2$/G composites; (b) Raman spectra of GO and CuFeO$_2$/G composites.

![Fig. 2](image2.png) (a) SEM images of (a) CuFeO$_2$ and (b) CuFeO$_2$/G composites; (c) TEM images of typical single CuFeO$_2$ crystal; and (d) HRTEM image of the edge of CuFeO$_2$ crystal and its corresponding Fourier transform.
In order to investigate the electrochemical performance contribution of graphene in CuFeO\textsubscript{2}/G composites, we also measured the cycling performance of pure graphene electrode tested under the same electrochemical condition. As we can see, the capacity of pure graphene electrode dramatically decreased from 1320 to 230 mAh g\textsuperscript{-1} after 10 cycles. The morphology of CuFeO\textsubscript{2}/G composites after 100 cycles at a current rate of 0.2 C is shown in Fig S4 (see ESI for details), which reveals that the structure of CuFeO\textsubscript{2} crystals is still kept during cycling process. The stabilized structures result in enhanced electrochemical performance. Compared with the previous reported CuFeO\textsubscript{2} as anode materials for LIBs,\textsuperscript{7b} the materials reported here exhibit higher specific capacity, better rate capability and cyclic stability.

EIS was used to illustrate the origin of the improved electrochemical performance of CuFeO\textsubscript{2}/G composites. The Nyquist plots \((Z' \text{ vs. } -Z")\) of CuFeO\textsubscript{2} crystals and CuFeO\textsubscript{2}/G composites were presented in Fig. 3 (d). The semicircle at high frequency due to a passivation layer formed which creates corresponding impedance at the surface of working electrode and electrolyte.\textsuperscript{24} The semicircle dominating in medium frequency describes the charge transfer impedance \((R_\text{ct})\) through the electrode/electrolyte interface, which is considered as a large proportion of overall cell’s kinetic impedance.\textsuperscript{42} The inclined line known as Warburg impedance, represents the \(Li^+\) ions diffusion/transport in the electrolyte to the electrode surface.\textsuperscript{43} It is obvious that the semicircle diameter for the CuFeO\textsubscript{2}/G composites is smaller than that of CuFeO\textsubscript{2} crystals, showing a lower \(R_\text{ct}\). In the low frequency region, the smaller inclination of CuFeO\textsubscript{2}/G composites is a further evidence of the faster \(Li^+\) ions diffusion/transport behavior.

The enhanced electrochemical performance of CuFeO\textsubscript{2}/G composites should be originated from their structure features. The graphene sheets in the composites function as conductive network to improve the conductivity and as structural buffer to maintain the structure integrity during cycling process. The structure of platelets/rings could enlarge the contact area between electrolyte and active material, shorten \(Li^+\) ions transport length, and the pores in the oxide rings can buffer the volume variation during lithiation/delithiation process.\textsuperscript{12} Thus, the synergetic effect of conductive graphene and CuFeO\textsubscript{2} hexagonal platelets/rings are responsible for the enhanced electrochemical performance of CuFeO\textsubscript{2}/G composites.

In summary, we developed a facile, one-pot, and low temperature hydrothermal route to prepare CuFeO\textsubscript{2}/G composites as feasible anode material for LIBs. The CuFeO\textsubscript{2}/G composites exhibit enhanced electrochemical performance with high specific capacity of \(-670\) mAh g\textsuperscript{-1}\textsuperscript{1} up to 100 cycles at a current rate of 0.2 C, good rate capability and cyclic stability. The enhanced electrochemical performance originated from the synergetic effect between graphene and CuFeO\textsubscript{2} hexagonal platelets/rings. Accordingly, we believe that the delafossite CuFeO\textsubscript{2} composites can be used as suitable anode candidate for LIBs and the preparation method could be extended to fabricate other delafossite-type oxides and graphene composites.

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Notes and references

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