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Hollow porous CuO/C composite microcubes derived from metal-organic framework templates for highly reversible lithium-ion batteries

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ABSTRACT

Hollow porous CuO/C composite microcubes are prepared by controlled pyrolysis of $[Cu_3(btc)_2]_n$ (btc = benzene-1, 3, 5-tricarboxylate) metal-organic frameworks (MOFs). SEM and TEM images indicate that the as-prepared CuO/C microcubes possess uniform appearance with hollow porous structures. Electrochemical measurements show that the hollow porous CuO/C composite microcubes deliver a highly reversible capacity of 510.5 mA h g^{-1} after 200 cycles at a current density of 100 mA g^{-1}. Due to its hollow porous structure and the enhanced conductivity of residual carbon, the rate performance delivers excellent reversible capacity of 232.78 mA h g^{-1} at a high current rate of 3.2 A g^{-1}. The recycled morphology could remain the original structure, further indicating that the microcubes are resistant to collapse and more suitable for lithium-ion batteries storage materials.

1. Introduction

The development of high-performance electrode materials is essential to lithium-ion batteries (LIBs) with high capacity and energy, which are widely utilized in many fields, such as new energy vehicles, portable electronics, smart device [1–5]. To date, graphite material is widely used as the anode material in LIBs and its limited theoretical capacity is about 372 mA h g^{-1} because of the formation of intercalated compound LiC_6 [6–8]. Traditional lithium storage materials still encounter serious capacity loss when charged-discharged at high rates because of the high polarization and slow diffusion of Li^+ ions and electrons in the active materials [9,10]. As a consequence, considerable effort has recently been focused on the development of alternative electrode materials that can provide higher capacity and rate performance in order to meet the growing demand of various consumer electronic devices [11–13]. Recently, metal oxides with hollow and porous features have received increasing attention because of their unique structures and properties that render them promising candidates in a wide range of applications, such as energy storage and conversion, catalysis, and biomedicine [14–17].

Metal organic frameworks (MOFs) are a novel class of porous materials consisting of metal ions coordinated with rigid organic molecules to form diverse architectures [18]. They have been proven to be promising precursors or sacrificial templates to construct the corresponding morphology inherited hollow metal oxides [19–23]. For example, Zeolitic Imidazolate Framework 67 (ZIF-67) has been applied for selective synthesis of Co_3O_4 hollow dodecahedra and $Zn_xCo_{3-x}O_4$ hollow polyhedra [20,21]. The composition-tunable multiple ball-in-ball hybrid metal oxides have also been fabricated by taking advantage of the unique reactivity and thermal behavior of spherical MOFs [22]. In recently years, CuO has drawn much attentions because of their various promising applications, such as gas sensors, catalysis, LIBs [24,25]. Considering that their application prospect and merits of hollow structure, CuO materials with various hollow nanostructures have been prepared. There are reports that CuO hollow nanoparticles synthesized by pyrolysis MOF-199 and CuO/Cu_2O composite hollow polyhedrons fabricated from MOF templates deliver long cycling life [26,27]. However, so far, the synthesis protocols for CuO or Cu_2O hollow nanostructures are still insufficient and the rate performance still remains to improve. Although copper oxide was easily prepared by decomposition MOF templates, the pure CuO or CuO/Cu_2O materials are poorer carriers for electronic. Therefore, the cycle and rate

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performance of copper oxides anode are restricted. In order to obtain superior electrochemistry performance, the conductivity of CuO or CuO/Cu_2O electrodes must be improved and the mainstream approach is to composite carbonaceous material. Fortunately, the cuprum and carbon exist in MOF-199 ($[Cu_3(btc)_2]_n$) and accurately controlled pyrolysis of the MOF-199, it maybe decompose to carbon substance and copper oxide. As a result, the enhanced conductivity of CuO electrode possesses preferable performance.

In this regard, we report a solvothermal method towards the synthesis of $[Cu_3(btc)_2]_n$, followed by a thermal accurately decomposition process to form hollow porous CuO/C composite microcubes by using MOF templates. The hollow porous structure provides an ion transfer tunnel for Li-ion insertion/extraction and the residual carbon provides a preferable electron transfer channel. As a result, when evaluated as anode materials, the as-synthesized hollow porous CuO/C composite microcubes exhibit excellent cycle performance and rate capability for LIBs.

2. Experiment details

2.1. Preparation of hollow porous CuO/C composite microcubes

All the chemicals were analytical grade and used without further purification. In this case, we obtained the copper benzene-1, 3, 5-tricarboxylate polyhedron ($[Cu_3(btc)_2]_n$) by a solvothermal method. In a typical synthesis, 41 mg $Cu(NO_3)_2 \cdot 3H_2O$ (AR, 99%), 1.902 g lauric acid and 20 mg benzene-1,3,5-tricarboxylic acid (btc, AR, 99%) were dissolved in 10 mL of butanol (AR, 99%). After being stirred vigorously for 10 min, the mixture was put into a 50 ml Teflon-lined stainless steel autoclave. The autoclave was treated at 140 °C and maintained for 3 h before cooled in air. The precipitates were isolated by centrifugation, washed with distilled absolute ethanol and water for several times to remove the possible residues, dried in vacuum, and kept for further characterization. The hollow porous CuO/C composite microcubes were obtained by thermal decomposition of $[Cu_3(btc)_2]_n$ in air at 350 °C for 0.5 h. Meanwhile, the hollow porous CuO microcubes were obtained by thermal decomposition of $[Cu_3(btc)_2]_n$ in air at 350 °C for 1 h and pristine CuO is achieved by directly thermal decomposition of $Cu(NO_3)_2 \cdot 3H_2O$ in air at 500 °C for 2 h.

2.2. Materials characterization

TGA and DSC (Diamond DMA, PerkinElmer Instruments) measurements were performed in oxygen stream from 25 °C to 1000 °C with a heating rate about 10 °C min^{-1}. Powder X-ray diffraction (XRD, X'Pert PRO, PANalytical B.V., The Netherlands) was performed with Cu Kα1 (45 kV, 40 mA, $10° < 2\theta < 90°$) in order to identify the crystalline phase of the materials. The Brunauer-Emmett-Teller (BET) specific surface area of the composites was measured by nitrogen adsorption at 77 K on a surface area and porosity analyzer (Autosorb-iQ, Quantachrome Instruments U.S.). The particle morphologies of the samples were examined with scanning electron microscopy (SEM, Nova Nano SEM 450, FEI, The Netherlands) and transmission electron microscopy (TEM, Tecnai G2 F30, FEI, The Netherlands).

2.3. Electrochemical measurements

For the preparation of anode sheets, a slurry was formed by mixing the active material (80 wt%), acetylene black (10 wt%) and binder (10 wt% polyvinylidene fluoride, PVDF, dissolved in *N*-methyl-2-pyrrolidone, NMP). Then the slurry was coated onto a copper foil current collector. The electrodes were dried under vacuum at 120 °C for 12 h and then punched and weighed. The mass loading of the electrode (CuO/C) is about 2.98 mg/cm^2 and the area of electrode is 0.50 cm^2. The batteries were assembled in a glove box under a high purity argon atmosphere. A celgard 2300 (polypropylene) was used as the separator and a lithium foil was used as anode. One molar of $LiPF_6$ dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1: 1 by volume) was used as the electrolyte. Cyclic voltammetry (CV, CHI 760D electrochemical workstation) was measured with electrochemical workstation at a scan rate of 0.1 mV s^{-1} between 0.01 V and 3.0 V. Charge-discharge performance of the cell was characterized at a current density of 100 mA g^{-1} between 0.01 V and 3.0 V (Land, China). Electrochemical impedance spectroscopic (EIS, CHI 760D electrochemical workstation) was studied with fresh batteries without any cycle in the frequency range from 10 mHz to 100 kHz.

3. Results and discussion

The entire synthetic process for hollow porous CuO/C composite microcubes are schematized in Fig. 1. First, lauric acid as an emulsifier combined btc with Cu^{2+}. Then the mixture reacted at high temperature by solvothermal process in an airtight container [28]. The specific formation mechanism of $[Cu_3(btc)_2]_n$ microcubes were investigated in previous literature (27). Finally, with an annealing treatment, hollow porous CuO/C composite microcubes could be readily obtained by a thermally induced oxidative decomposition process.

Fig. 2 shows the thermal behavior of $[Cu_3(btc)_2]_n$ investigated by thermogravimetric analysis TGA-DSC. The first weight loss about 21.25% up to a temperature 200 °C is attributed to the removal of sparingly volatile solvent butanol and water, which effectively indicates the $[Cu_3(btc)_2]_n$ has a good thermal stability [27]. Once above 240 °C, a strong exothermic peak in DSC curve were observed and there is a weight loss about 52.81% from TGA curve, which could be attributed to the pyrolysis of $[Cu_3(btc)_2]_n$ porous framework and organic molecules. After that, there is a little weight loss (10.21%) after 450 °C, the most reasonable explanation is the oxidation of carbon which comes from MOFs pyrolysis. It is quite important that the residual carbon is an electron carrier to enhance the conductivity of the CuO/C electrode. Therefore, in present case, the pyrolysis of $[Cu_3(btc)_2]_n$ at 350 °C for 0.5 h can yield highly crystalline CuO phase with black color. TGA-DSC analysis indicates that the chemical compositions of the material are CuO and C with the ratio of CuO/C of 1.5: 1.

The detailed morphological and structural features of hollow porous CuO/C composite microcubes were further characterized by field emission scanning electron microscope (FSEM) and transmission electron microscopy (TEM). The $[Cu_3(btc)_2]_n$ MOFs are uniform cubes (Fig. 3a). A high-magnified FESEM image (Fig. 3b) indicates that these $[Cu_3(btc)_2]_n$ cubes possess well-defined size and rhombic shape. After the pyrolysis of $[Cu_3(btc)_2]_n$ microcubes, the cube morphology could still be well-preserved and it seems to be boxes with edges and corners distinct (Fig. 3c). The cube surface is coarse and composed of closely packed small nanoparticles with porous structure, as revealed in a high resolution FESEM image (Fig. 3d). The hollow interior of CuO microcubes was validated by TEM analysis. There is a sharp contrast between the shells (light) and interior cavities (shadow) of the cube (Fig. 3e). The highly symmetric cube shell framework constructed by small subunits and the interparticle mesopores distributed throughout the shell could be observed more explicitly from the magnified TEM image (Fig. 3f). The surface area is appreciable (16 m^2/g) and the pore size is 4.07 nm (Fig. S1), which provide more electrochemically active surface sites for Li-ions storage. The more pictures with different magnifications are shown in Fig. S2. The selected area electron