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Carbon coated copper sulfides nanosheets synthesized via directly sulfurizing Metal-Organic Frameworks for lithium batteries

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ABSTRACT

Carbon coated copper sulfides nanosheets, denoted as C@$Cu_{1.96}S$, are successfully prepared via directly annealing Metal-Organic Framework (HKUST-1) and commercial sulfur powder. As cathode materials for lithium batteries, the as-prepared C@$Cu_{1.96}S$ nanosheets deliver high reversible capacity, good capacity retention and superior rate capability.

1. Introduction

Lithium batteries have been widely applied in areas of portable electrons, digital communication and hybrid electronic vehicles [1,2]. Recently, metal sulfides, such as Co_9S_8, FeS_2 and CuS, have been investigated as electrode materials for lithium battery, owing to their high theoretical energy densities and good electronic conductivity [3–7]. However, the rapid capacity fading caused by the drastic volume expansion and the dissolution of lithium polysulfides during charge/discharge cycling restrict its electrochemical performance [8]. In order to overcome the issue, many efforts have made by designing nanostructures to alleviation the volume expansion and introducing coating to restrict the lithium polysulfides dissolution [7,9,10]. For example, Zhou et al. [9] reported that sub-10 nm copper sulphide rods exhibit excellent cycle performance (250 cycles with a sustainable capacity of 390 mA h g^{-1}). And Meng et al. [10] have fabricated Cu_2S-single walled carbon nanotube nanocomposites for high performance Li ion battery. However, multi-step reactions are usually needed to prepare electrode materials with both nanostructure and coating.

Metal-Organic Frameworks are a new class of crystalline compound created from the supramolecular assembly of metal ions with rigid organic molecules. Inspired by well-dispersed metal ions, abundant carbon containing linkers within their porous structure, MOF have been used as a effective precursors for the fabrication of carbon materials and metal oxides with novel nanoarchitectures or porosities [11,12].

In the present work, carbon coated copper sulfides nanosheets were successfully synthesized via one-step sulfurizing Metal-Organic Framework. The electrochemical properties of as-prepared C@$Cu_{1.96}S$ nanosheets as cathode materials were investigated.

2. Experimental

2.1. The synthesis of copper sulfides nanosheets

All chemicals are purchased from Sinoregent and used as obtained. HKUST-1 is according to reference with modification [13]. Firstly, 2.5 g $Cu(NO_3)\cdot 3H_2O$ and 5 g 1,3,5-benzenetricarboxylic acid were dissolved in 250 ml N,N-Dimethylformamide (DMF) under continuous magnetic stirring. Then the resulting solution was transfer to a polytetrafluoroethylene container, and heated in an oven at 75 °C for 24 h. After cooling to room temperature, the obtained products were separated via centrifugation and washed with DMF, dried at 100 °C for 12 h. The resulting powders were mixed with commercial sulfur powder (the weight ratio 1:2) and annealed in nitrogen atmosphere at 650 °C for 2 h to obtain

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C@$Cu_{1.96}S$ nanosheets.

2.2. Material characterization

X-ray diffraction (XRD using a Rigaku Dmaxrc diffractometer) was used to characterize crystallographic phases of the as-synthesized products. A JEOL JEM-2100 TEM was utilized to evaluate the microstructure of carbon doped $Cu_{1.96}S$ composite. the morphology and size of samples were determined by a scanning electron microscope (SEM, Zeiss SUPRA 55). Thermogravimetric analysis (TGA) was taken on a Mettler-Toledo TGA/SDTA851e Thermo Analyzer from 30 to 1000 °C in air atmosphere with a heating rate of 5 °C min^{-1}. BET analysis of the products was conducted by Micromeritics Automatic Surface Area Analyzer Gemini 2360 at 77 K. the specific surface areas were calculated using Brunauer Emmett Teller (BET) method. Raman spectra were measured on a Horiba Jobin-YVON co-focal laser Raman system with He-Ne 632 nm laser as the excitation source.

2.3. Electrochemical characterization

In order to evaluate the electrochemical performance of C@$Cu_{1.96}S$ nanosheets, 2016 coin-type were assembled under high purity argon atmosphere in glove box. The mixture of active material (C@$Cu_{1.96}S$, 60 wt%), carbon black (20 wt%) and polyvinylidene fluoride (PVDF, 20 wt%) were constantly mixed and stirred to form slurry. the electrode for cathode performance was fabricated by doctor-blade method on the Al-foil current collector. 1 M Li[$N(SO_2CF_3)_2$] in DME/DIOX were used as electrolyte. Galvanostatic charge-discharge tests of the cells were carried out between 0.8 and 3 V at various rates (1C=500 mA h g^{-1}). The electrochemical impedance spectroscopy (EIS) measurement was performed on a CHI 660E (Shanghai China) in a frequency range from 0.01 Hz to 1 M Hz.

3. Result and discussion

Fig. 1(a) shows the XRD pattern of the as-synthesized C@$Cu_{1.96}S$ nanosheets. All diffraction peaks (expect for one peaks originated from graphitic carbon) can be index to tetragonal $Cu_{1.96}S$ (JPCDS NO. 29-0578), indicating that Metal-Organic Framework (HKUST-1) could be fully converted to C@$Cu_{1.96}S$ composite after sulfurizing treat at 650 °C. For further proving the existence of carbon in C@$Cu_{1.96}S$ composite, Raman measurement was conducted, from the figure we can see two broad peaks located at 1365 and 1576 cm^{-1} (as shown in the Fig. 1(b)). These peaks can be attributed to typical D and G bands of carbon [14], which proved the existence of carbon. To further determine $Cu_{1.96}S$ content of the composite materials, TGA analyses were performed and the results are shown in Fig. 1(c). The initial mass uptake about 300 °C can be assigned to the following reaction: $Cu_2S + 1.5O_2 \rightarrow Cu_2O + SO_2$ and $Cu_2O + O_2 + SO_2 \rightarrow CuO \cdot CuSO_4$. The mass drop between 600 and 750 °C results from $CuO \cdot CuSO_4 \rightarrow 2CuO + SO_2 + 0.5O_2$, $CuO \rightarrow 0.5Cu_2O + 0.25O_2$ and the oxidation of carbon [10]. Based on these analyses, the ~64% weight remaining from the C@Cu 1.96 S sample reveals a content of 71 wt% $Cu_{1.96}S$ in the composite. The surface areas of C@$Cu_{1.96}S$ nanosheets were measured using BET

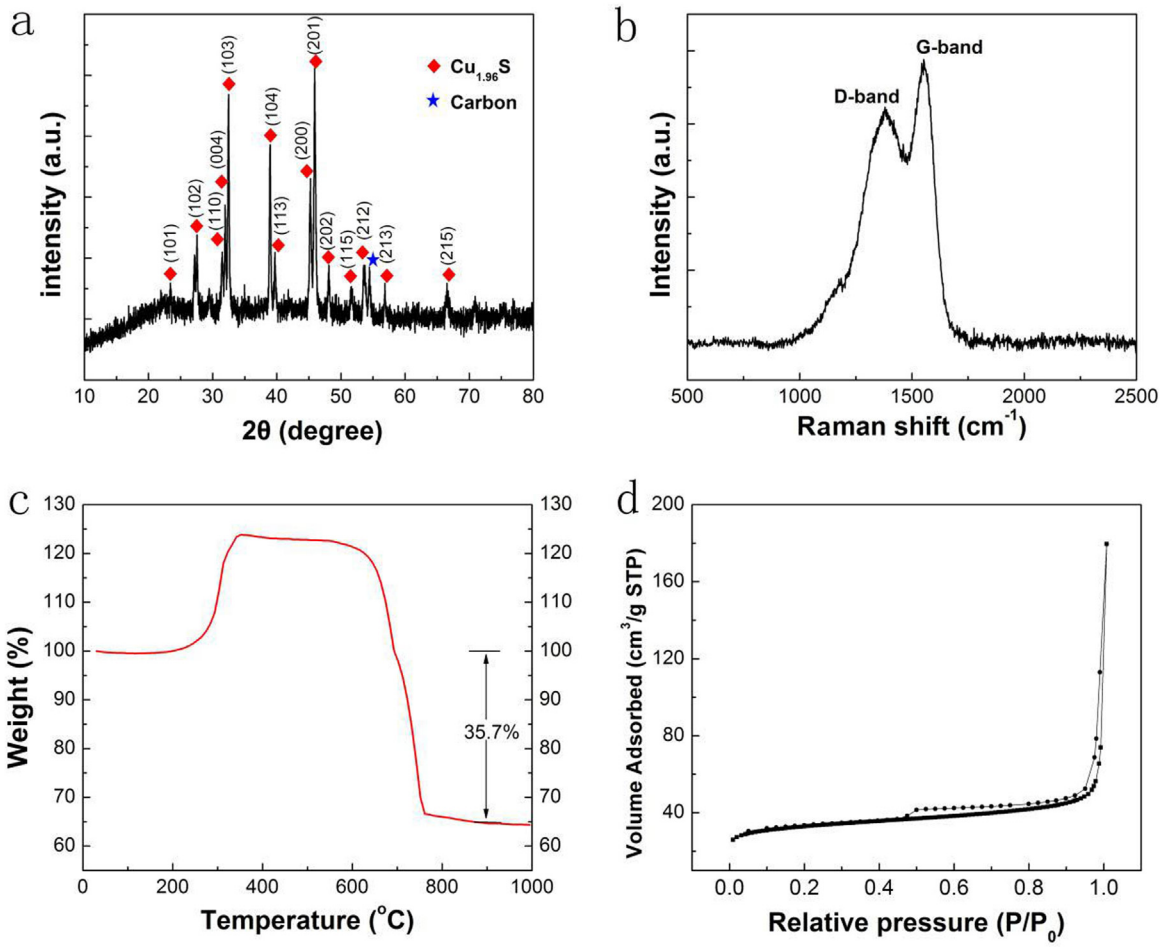

Fig. 1. XRD pattern (a) and Raman spectra (b) and TGA curves (c) and N_2 adsorption-desorption isotherm of C@$Cu_{1.96}S$(d).