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Metal-organic framework-derived carbon coated copper sulfide nanocomposites as a battery-type electrode for electrochemical capacitors

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ABSTRACT

Metal-organic framework (MOF)-derived carbon-coated metal sulfides are a popular research area for energy storage, owing to their highly reactive nature and universal electrochemical activity. A simple and efficient method for the preparation of carbon-coated copper sulfide via a calcining-hydrothermal process using an MOF template is presented in this paper. The transmission electron microscope (TEM) imaging indicates that the cobble-like Cu_7S_4 nanopolyhedra are ~100 nm in size, and are interconnected by amorphous carbon. Electrochemical analysis shows that the Cu_7S_4/C electrode possesses the highest capacitance, 321.9 F g^{-1} (80.5 mAh g^{-1} in capacity), at a current density of 0.5 A g^{-1}, and achieves nearly 78.1% capacitance retention after 3000 cycles, suggesting its holds promise for application in battery-type electrode materials for supercapacitors.

1. Introduction

Supercapacitors are considered attractive energy storage sources because of their high power density, fast charge-discharge rate, and long cycle life [1,2]. Copper sulfide, as a supercapacitor electrode material, has received particular attention due to its high electronic conductivity, variety of structures, and complex valence status [3]. To achieve good electrochemical performance, well-modified morphologies of carbon-coated copper sulfide are needed. Thus far, metal-organic frameworks (MOFs) have been used as effective self-templates to prepare highly porous carbon materials and metal sulfides [4–7]. Carbon-coated copper sulfide composites are synthesized by directly calcining MOF template with sulfur powder, and it has already been used for energy storage [8–10]. While these reports illustrate its potential for the development of high-performance electrode materials, a low specific capacitance was demonstrated (~155 F g^{-1} at 1 A g^{-1}). It is still a challenge to obtain the desired electrochemical performance from MOF-derived carbon-coated copper sulfide.

We report a facile synthesis of carbon-coated copper sulfide via a two-step calcining-hydrothermal process on a widely used Cu-MOF (nHKUST-1). As expected, the obtained Cu_7S_4/C nanocomposites exhibit excellent electrochemical performances when used as a battery-type supercapacitor electrode material.

2. Experimental

The synthesis of Cu-MOF (nHKUST-1) was performed through a hydrothermal approach in accordance with the procedures outlined in previous literature (materials and experimental details are provided in Supporting Information) [11]. Then, the prepared nHKUST-1 (0.2 g) was annealed in a nitrogen atmosphere at 650 °C for 2 h to obtain the brown-powder precursor. Subsequently, the precursor and thioacetamide (0.36 g) were dissolved into 80 ml of ethanol with ultrasonic string. The resultant solution was transferred to a 100 ml Teflon-lined autoclave and heated at 120 °C for 6 h. Thus, a black powder was obtained, which was then filtered, rinsed with ethanol, and dried overnight.

The as-prepared samples were characterized by X-ray diffraction (XRD, D/MAX-RB with Cu Kα radiation), scanning electron microscopy (SEM, Nova450), Raman spectra (Raman, Horiba

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YVON), thermogravimetric analysis (TGA, NETZSCH 449F3), transmission electron microscopy (TEM, FEI Tecnai G2 F20), and X-ray photoelectron spectroscopy (XPS, Escalab250).

The electrochemical performances of the as-prepared sample were measured using a standard three-electrode system in a 1 M H_2SO_4 electrolyte solution with Pt wire and an Ag/AgCl electrode as the counter and reference electrode, respectively. The working electrodes were fabricated through a typical coating process with a mass loading of 3 mg cm^{-2} [12]. Cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) were conducted using a CHI 760E electrochemical workstation.

3. Results and discussion

First, nHKUST-1 was fabricated by a facile hydrothermal method. Fig. 1(a) shows the XRD pattern of the as-synthesized nHKUST-1. All the nHKUST-1 diffraction peaks are consistent with the simulated pattern (based on crystal data from CCDC: 112954), indicating the high purity. In the SEM image in Fig. 1(b), well-defined smooth-surfaced polyhedral crystals 100–300 nm in size are observed.

After oxidation and sulfidation, the copper ions within nHKUST-1 were transferred to copper sulfide (Cu_7S_4) nanoparticles, while the organic ligand was carbonized to amorphous carbon. Fig. 2(a) shows the XRD pattern of the obtained Cu_7S_4/C nanocomposites; all the diffraction peaks could be well matched to that of Cu_7S_4 (PDF: 23-0958), indicating that nHKUST-1 had been fully converted to Cu_7S_4/C. Next, Raman measurement was conducted to obtain further evidence of the existence of carbon in the Cu_7S_4/C nanocomposite. Two main broad peaks are observed in Fig. 2(b), located at 1347 and 1584 cm^{-1}. These peaks are associated with the D-band (disordered carbon, 1347 cm^{-1}) and G-band (graphitized carbon, 1584 cm^{-1}) [8–10], proving the existence of carbon. The other two main peaks, located at 281 and 473 cm^{-1}, are associated with the Cu-S and S-S, proving the existence of Cu_7S_4 [13–15]. To further determine the carbon content of the Cu_7S_4/C nanocomposite materials, TGA analyses were performed, and the

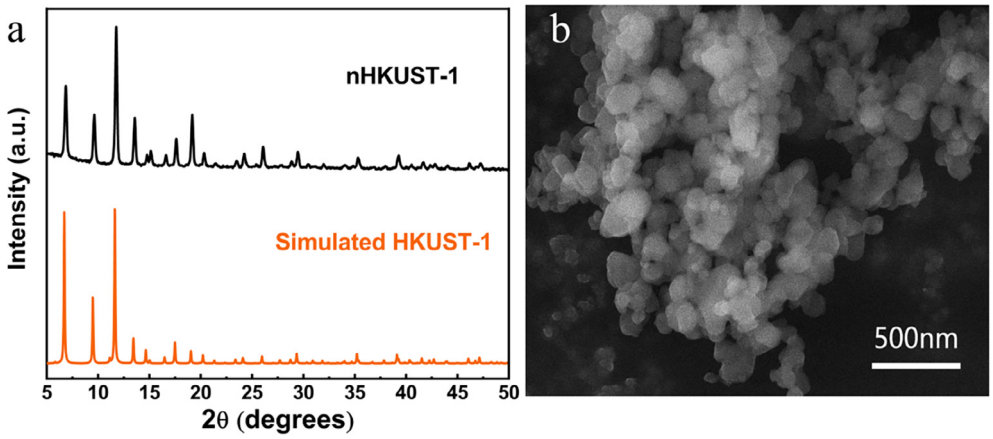

Fig. 1. (a) XRD pattern, (b) SEM image of Cu-MOF (nHKUST-1).

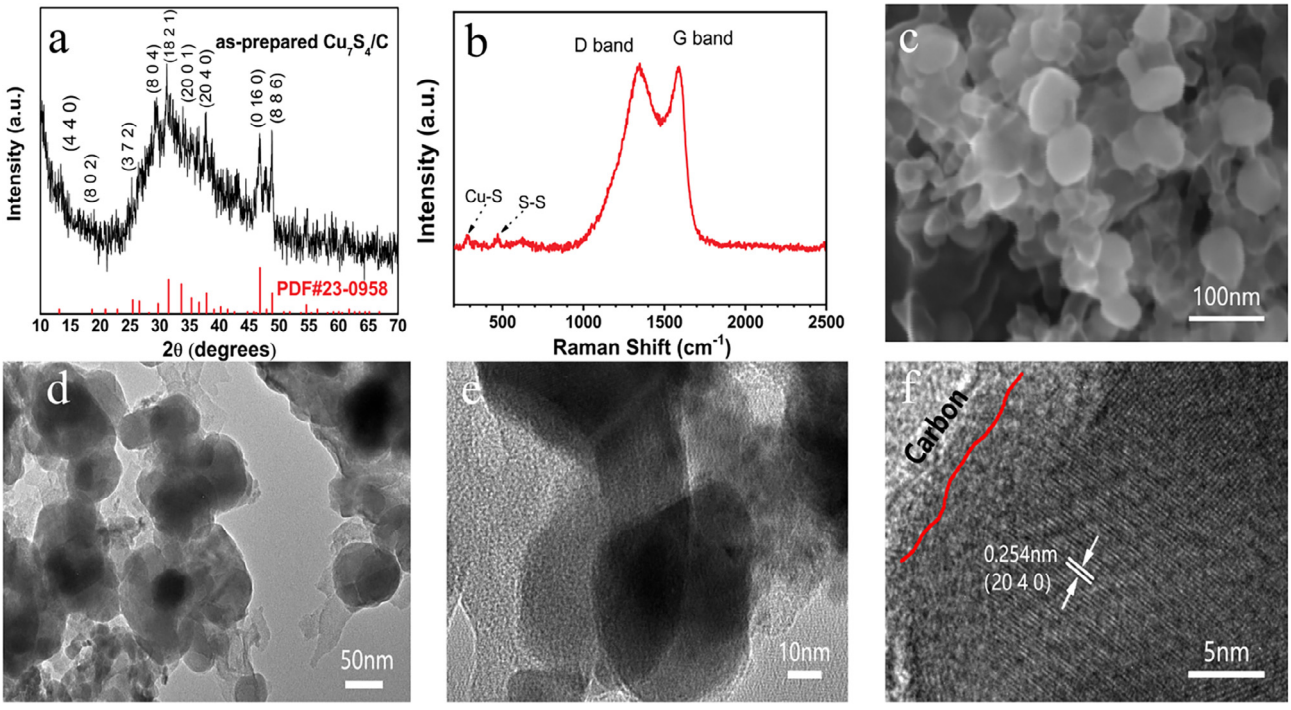

Fig. 2. (a) XRD pattern, (b) Raman spectra, (c) SEM, (d, e) TEM and (f) HRTEM images of Cu_7S_4/C nanocomposites.