Full Length Article

Quasi-hexagonal $Cu_{1.5}Mn_{1.5}O_4$ nanoplates decorated on hollow CuO by Kirkendall effect for enhancing lithium storage performance

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A R T I C L E I N F O

A B S T R A C T

Constructing a hierarchical heterogeneous composite is deemed as an effective way to solve the current problems of metal oxides as lithium ion batteries' anodes. In this work, we simultaneously designed the heterogeneous component and structure of the novel hybrid based on Kirkendall effect. The composite was composed of quasi-hexagonal $Cu_{1.5}Mn_{1.5}O_4$ nanoplates as a shell and CuO with voids as a core. The hybrids were characterized by using XRD, FTIR, TEM and SEM. It was found that the heating rate greatly influences the combination form of $Cu_{1.5}Mn_{1.5}O_4$ and CuO. The quasi-hexagonal $Cu_{1.5}Mn_{1.5}O_4$ nanoplates were assembled into branch-like shell decorated on the CuO surface under the low heating rate. However, the high heating rate led to a compact $Cu_{1.5}Mn_{1.5}O_4$ shell, although the shell was also assembled by quasi-hexagonal nanoplates. The reasonable formation mechanism of the unique component and structure was proposed. Such a hybrid with the branch-like shell exhibited the best lithium storage performance. The improved electrochemical performance can be attributed to the unique component and structure. Typically, the inside voids can alleviate the volume change and the hierarchical shell can provide much contact and reaction sites. This work not only opens a new view in constructing heterogeneous hybrid with unique structure by Kirkendall effect, but also can be expanded for many other structure-based applications, such as energy storage, sensors, and heterogeneous catalysts.

1. Introduction

In the past two decades, metal oxides have been deemed as the promising alternative anode material for lithium ion batteries owing to their high theoretical capacity compared to traditional anode graphite [1–3]. Many metal oxides, such as CuO [4], CoO [5], Co_3O_4 [6], Fe_3O_4 [7], NiO [8], MnO [9], have been studied, but their lithium storage performance needs to be improved because the intrinsic low electronic conductivity and large volume variation during the lithiation–delithiation process limit their electrochemical properties. Generally speaking, there are two dominated types of strategies to solve the above problems. One is the construction of metal oxides' structure on size and/or dimension [2,10]. By decreasing the bulk size into nanosize, the transport length of lithium ions can be shortened and the expansion stress can be weakened. Besides, a hierarchical structure can make more reaction active sites which enhances the corresponding electrochemical performance [11]. However, the products with a nanosize always possess a low density which hinders the improvement of volumetric electrochemical performance [12]. The other method

is to form a heterogeneous hybrid composite by integrating one with other metal oxides or carbonaceous nanomaterial [13,14]. In this regard, many heterogeneous metal oxides composites, such as $Fe_2O_3@NiCo_2O_4$ [15], $SnO_2-Fe_2O_3$ [13], CuO@NiO [16], $CuO@CuFe_2O_4$ [17], were synthesized which showed the enhanced lithium storage performance compared to single metal oxide. The enhanced performance benefits from the synergetic effect between the heterogeneous components. Besides, the combination form of the heterogeneous components also plays an important role in the electrochemical performance because it determines the nanostructure of final composites.

The Kirkendall effect is a representative phenomenon of unequal matter inter-diffusion, which usually accompanies with the formation of voids when the outside diffusion is faster than the inside one [18–20]. This effect is common in metallurgy and not desirable in alloying and welding if the Kirkendall voids are generated [21]. Since Yin et al. [18] reported a conversion from metal nanoparticles to the hollow oxides and chalcogenides through the Kirkendall effect in nanoscale, many researchers have designed hollow structures based on Kirkendall effect for various applications, such as lithium ion batteries [22], sodium ion batteries [23], catalyst [24]. For instance, Cho and et al. reported a 1-D Fe_2O_3/Se nanorods composite, which shows an excellent discharge

capacity of 1456 mAh g^{-1} at 1.0 A g^{-1} [25]. Park and et al. synthesized a Janus-structured mutually doped SnO$_2$-Co$_3$O$_4$ composite with an extraordinary cycling performance (1058.7 mAh g^{-1} after 1000 cycles at 1.0 A g^{-1}) [26]. However, most reports only focus on the inner hollow structure and there is rare work on the outside structure. Besides, for metal oxides, only a few references report the multi-metal oxides related to the Kirkendall effect. For instance, Fan et al. [19] synthesized the spinel ZnAl$_2$O$_4$ nanotube and Wang et al. [24] produced Fe$_2$(MoO$_4$)$_3$ nanotubes. In our previous work, we found that the spinel multi-metal oxide could improve electrochemical performance of individual metal oxides by forming the composite with them [17]. Therefore, it is interesting to use the Kirkendall effect to develop composites with special inside and outside structures by using the components of multiple metal oxides.

Herein, we have simultaneously engineered the metal oxides' component and structure by the Kirkendall effect. For the first time, a hierarchical hybrid of CuO and Cu$_{1.5}$Mn$_{1.5}$O$_4$ was synthesized, in which the voids existed in the inner core of CuO and the quasi-hexagonal Cu$_{1.5}$Mn$_{1.5}$O$_4$ nanoplates decorated on the outside of CuO cores. It is found that the heating rate is related to the shell's structure. Typically, when a low heating rate was applied, the hybrid possessed a branch-like Cu$_{1.5}$Mn$_{1.5}$O$_4$ shell which was assembled by the quasi-hexagonal nanoplates. While the high heating rate led to a compact shell, although the shell was also composed of the quasi-hexagonal Cu$_{1.5}$Mn$_{1.5}$O$_4$ nanoplates. Moreover, when evaluating their lithium storage performance, the hybrid obtained at the low heating rate exhibited the best electrochemical properties. The enhanced performance can be attributed to the special components and their combination form.

2. Experimental

2.1. Synthesis

The precursor of the target hybrid was obtained by wet-chemical method according to our previous reported work [27]. Typically, 80 mL ethanol dispersive solution of Cu$_2$O (400 mg) was prepared. Then, the NaCl aqueous solution (5 mL, 0.328 g) was added into the above dispersive soltuion. After stirred for 15 min, 277 mg of MnCl$_2$·4H$_2$O was dissolved in 80 mL ethanol, and the obtained solution was quickly poured into the previous dispersive solution of Cu$_2$O. The mixture was stirred for 10 h. Then, the precursor was collected by centrifugation, washed with ethanol and water, and dried in vaccum oven at 50 °C for 6 h. Subsequently, the target products were obtained by calcining the precursor at 550 °C for 6 h in air with different heating rates (1, 2 and 5 °C min^{-1}). In order to distinguish easily, the target products were termed as CuO@Cu$_{1.5}$Mn$_{1.5}$O$_4$-T1, CuO@Cu$_{1.5}$Mn$_{1.5}$O$_4$-T2 and CuO@Cu$_{1.5}$Mn$_{1.5}$O$_4$-T5, respectively, where the suffix of T1, T2 and T5 represents the heating rate of 1, 2 and 5 °C min^{-1}, respectively. As a comparison, the pure CuO was prepared by calcining the Cu$_2$O at the heating rate of 1 °C min^{-1}.

2.2. Characterization

The crystalline structure and component of samples were investigated by X-ray diffraction (XRD; Bruker, D8 Advance) patterns with a scan rate of 2 ° min^{-1} and Fourier transform infrared (FTIR; MB154S) spectra using the pressed KBr pellets. Scanning electron microscopy (SEM; FEI, Quanta 250F) and Transmission electron microscopy (TEM; JEOL, JEM-2100) were conducted to study the morphology of the samples. The elemental mapping images and energy dispersive X-ray (EDX) spectra were collected by the EDX

spectrometer which were installed in the TEM (Tecnai G2 F30 S-TWIN) and SEM, respectively.

2.3. Electrochemical measurements

All the electrochemical tests were carried out by assembling a coin cell (CR2016) which consisted of the working electrode, separator (Celgard 2400), electrolyte and lithium foil (reference and auxiliary electrode) at room temperature. The working electrode was prepared by loading the active material, conductive carbon black and polyvinylidene fluoride with a mass ratio of 70:20:10 on the copper foil. The loading mass of active material was around 1.0 mg cm^{-2}. The electrolyte was composed of 1 M LiPF$_6$ and diethyl carbonate/dimethyl carbonate/diethyl carbonate (weight ratio: 1:1:1). Cyclic voltammetry (CV, CHI 760D, Chenhua, Shanghai) was conducted under a scan rate of 0.1 mV s^{-1} between 0.01 and 3.00 V. Electrochemical impedance spectrum (EIS) was measured with AC amplitude 5 mV in a range of 100 kHz to 0.01 Hz at the cell's open circuit potential. Galvanostatic discharge/charge measurement was implemented on a Land CT2001 battery test system at the potential range of 0.01–3.00 V.

3. Results and discussion

According to our previous work, the precursor consisted of Cu$_2$O core and a kind of amorphous Mn-based compound shell [27]. By heating the precursor in air with different heating rate, the target products were obtained. In order to investigate the chemical component and structure of the target products, XRD measurement was conducted. As shown in Fig. 1, all the peaks of CuO@Cu$_{1.5}$-Mn$_{1.5}$O$_4$-T1, CuO@Cu$_{1.5}$Mn$_{1.5}$O$_4$-T2 and CuO@Cu$_{1.5}$Mn$_{1.5}$O$_4$-T5 are assigned to CuO (JCPDS card no. 80-1917) and Cu$_{1.5}$Mn$_{1.5}$O$_4$ (JCPDS card no. 70-0260). No other peaks of residues or contaminants were found, indicating the high purity of the prepared products. The peaks of pure CuO are in accordance with the standard peaks of CuO (JCPDS card no. 80-1917). Moreover, the peaks of Cu$_{1.5}$-Mn$_{1.5}$O$_4$ in CuO@Cu$_{1.5}$Mn$_{1.5}$O$_4$-T5 were more intense than those in the other two hybrids. But, CuO@Cu$_{1.5}$Mn$_{1.5}$O$_4$-T1 and CuO@Cu$_{1.5}$Mn$_{1.5}$O$_4$-T2 have the almost same peak intensity of Cu$_{1.5}$Mn$_{1.5}$O$_4$. It means the Cu$_{1.5}$Mn$_{1.5}$O$_4$ crystal in CuO@Cu$_{1.5}$-Mn$_{1.5}$O$_4$-T5 has a more crystal degree owing to a higher heating rate.
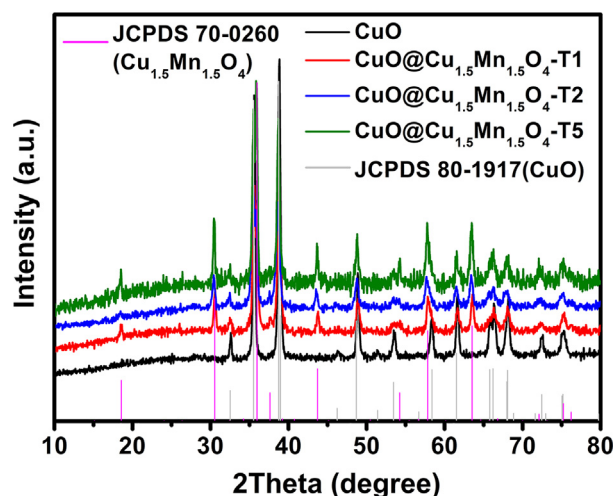
Fig. 1. XRD patterns of CuO, CuO@Cu$_{1.5}$Mn$_{1.5}$O$_4$-T1, CuO@Cu$_{1.5}$Mn$_{1.5}$O$_4$-T2 and CuO@Cu$_{1.5}$Mn$_{1.5}$O$_4$-T5.