

Short communication

Preparation of Cu₂O particles with different morphologies and their application in lithium ion batteries

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Abstract

For the first time Cu₂O particles with different morphologies are synthesized by adopting a polyol process performed at different temperatures. SEM and TEM show that the samples obtained at 140 and 160 °C present a core-shell structure. XRD measurements indicate that both samples exhibit better crystallinity compared with the samples obtained at 120 °C. Results from charge–discharge experiments and cyclic voltammograms (CV) reveal that morphology and crystallinity play important roles in determining the electrochemical performance of Cu₂O samples.

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1. Introduction

Cuprous oxide has attracted great interest of researchers because it is a p-type semiconductor and regarded as a promising material for applications in solar energy conversion and catalysis [1,2]. Recently, it was studied as a novel anode material with high capacity and good capacity retention meeting the needs of further development of lithium ion batteries since it is nontoxic and abundant in nature [3–6].

It is well known that morphology is an important factor in determining the physical and chemical properties of particles. Thus morphology-controlled synthesis has moved into focus. A lot of studies reported that electrode materials with special morphologies exhibit excellent electrochemical performance in lithium ion batteries by adopting hard templates or surfactants, including nano-scaled [7], core-shell [8,9] and hollow structured materials [10]. Here we report a facile method to synthesize Cu₂O samples with different morphologies by adopting a polyol process at different temperatures. Samples prepared at 140 and 160 °C exhibit core-shell structure. As far as we know, this is

the first report on the synthesis of core-shell structured Cu₂O particles without any template or surfactant.

2. Experimental

Cuprous oxide particles were prepared according to the following procedure. A 0.1 mol l⁻¹ solution of copper nitrate trihydrate (Cu(NO₃)₂·3H₂O) precursor was prepared by adding Cu(NO₃)₂·3H₂O to ethylene glycol (EG) under stirring. The solution was heated to 120, 140 and 160 °C, respectively, and further refluxed for 3 h. Magnetic stirring was continuously applied throughout the entire process of reduction and particle growth. Finally, the Cu₂O particles were separated from solution by centrifugation and washed with deionized water and alcohol to remove the residual glycol. Cu₂O particles were identified using a powder X-ray diffractometer with monochromatized Cu K α radiation (Bruker D8 Advance Spectrometer). Morphological observation was done by transmission electronic microscopy (TEM, JEOL JEM 2011) and scanning electron microscopy (SEM, Philips XL 300).

Electrochemical performance of electrodes was evaluated by assembling model coin-type cells using lithium foil as a counter and reference electrode, Celgard 2400 as a separator, and 1 mol l⁻¹ LiPF₆ solution in EC/DMC/DEC (1:1:1, w/w%) as an electrolyte. Capacity measurements for Cu₂O particles were carried out at 0.1 mA cm⁻² in the voltage range of 0–3 V. The

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working electrodes were prepared by mixing Cu_2O active material, acetylene black (AB) and poly(vinylidene fluoride) (PVDF) at a ratio of 85:10:5 (w/w%). The mixture was coated onto a copper foil. After drying, the coated foils were cut into pellets. Prior to assembling into coin-type model cells under argon atmosphere in a glove box, all the electrode pellets were dried overnight under vacuum at 120°C .

Cyclic voltammetric (CV) behavior was studied at room temperature using the model cells. CV measurement was carried out in the voltage range of 0–3 V at a scanning rate of 0.1 mV s^{-1} .

3. Results and discussion

The morphologies of Cu_2O samples prepared at different temperatures are shown in Fig. 1. From the SEM micrographs, it is obvious that a Cu_2O sample prepared at 120°C contains small flakes and large particles of irregular morphology, which are aggregates of smaller particles. Samples synthesized at 140 and 160°C are spherical, and their average diameter is about 2.5 and $1 \mu\text{m}$, respectively. Fig. 1(b) shows clearly the core-shell structure of the sample prepared at 140°C . Further investigation of samples prepared at 140 and 160°C was done with TEM. Fig. 2 clearly displays the core-shell structure morphology of Cu_2O samples synthesized at 140 and 160°C . The shell thickness is 420 and 120 nm , respectively. To our knowledge this is the first report on Cu_2O with core-shell morphology prepared without any template or surfactant although the formation mechanism is still unknown.

Fig. 3 shows X-ray diffraction patterns of Cu_2O samples prepared at different temperatures. The peak positions of all the samples are in good agreement with those for Cu_2O powder obtained from the International Center of Diffraction Data card (ICDD, formerly JCPDS) [11]. The pattern of each sample indicates that the intensities of the diffraction peaks for the samples prepared at 140 and 160°C are enhanced in comparison with those for the sample prepared at 120°C , implying higher crystallinity.

Although all the prepared samples contain crystalline cuprite, their electrochemical performance varies greatly with synthesis temperature. The first discharge and charge curves of Cu_2O electrodes in $1 \text{ mol l}^{-1} \text{ LiPF}_6 \text{ DEC/EC/DMC}$ (w/w/w: 1/1/1 wt.%) are illustrated in Fig. 4. The discharge capacity of Cu_2O samples prepared at 120 , 140 and 160°C are 351 , 589.2 and 604 mAh g^{-1} , respectively. The discharge curves for samples prepared at 140 and 160°C are similar and exhibit an abrupt drop at about 1.25 V , followed by a smooth decrease to 0.7 V . However, the discharge profile of the Cu_2O sample prepared at 120°C is quite different, with a steeper and shorter gradient from 1.25 to 0.7 V compared with the discharge profiles for the samples prepared at 140 and 160°C , respectively. The reversible capacity of Cu_2O particles synthesized at 160°C (242 mAh g^{-1}) is much higher than that of the samples prepared at 140°C (88.9 mAh g^{-1}) and 120°C (50.5 mAh g^{-1}). During charging of the sample prepared at 160°C , a slow slope change exists around 2.0 V , however, there is no slope but a rapid rise around 2.0 V for the samples prepared at 120 and 140°C . Different crystallinities caused by the different temperatures are conceivable

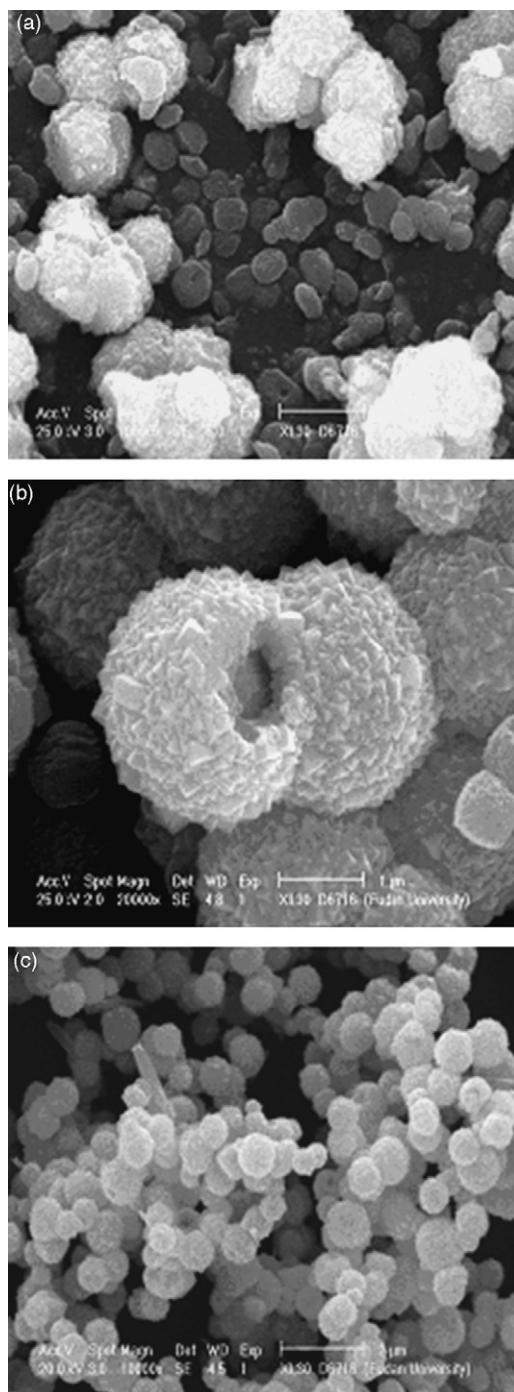
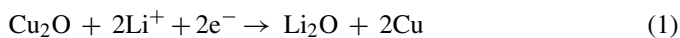


Fig. 1. SEM micrographs of Cu_2O particles prepared at different temperatures: (a) 120°C ; (b) 140°C ; (c) 160°C .

major reasons; further evidence is needed. When the crystallinity is high, the charge plateau appears.

According to the reports by Tarascon et al. during the discharge process the reaction between 1.25 and 0.7 V is described as [12]



The capacity below 0.7 V is ascribed to the reduction of electrolyte solution and formation of a SEI-like (solid electrolyte interface) organic layer. During the charging

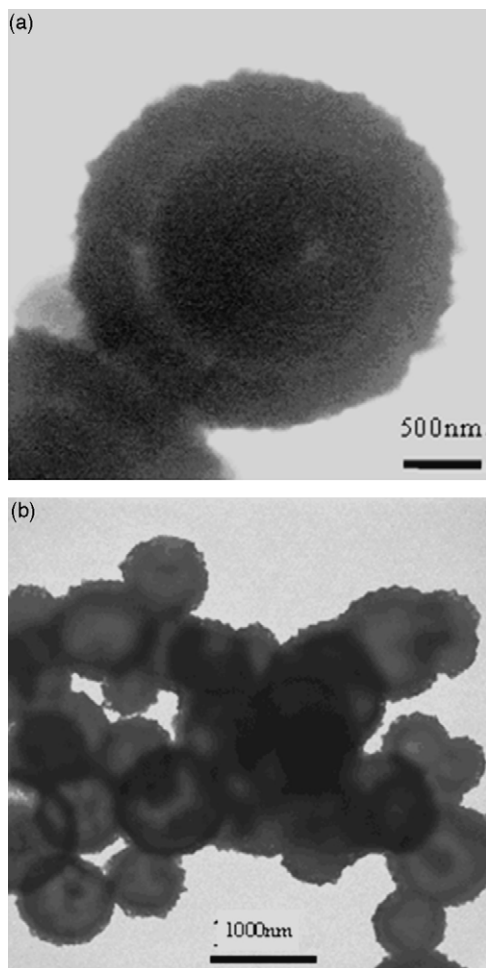


Fig. 2. TEM micrographs of core-shell structured Cu_2O particles prepared at different temperatures: (a) 140°C and (b) 160°C .

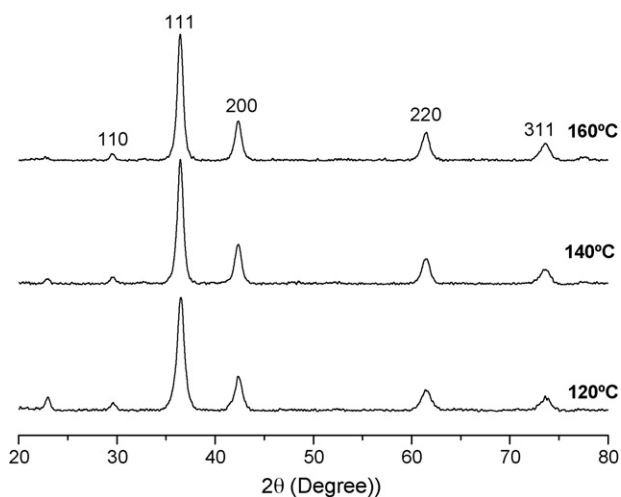


Fig. 3. X-ray diffraction patterns of crystalline Cu_2O prepared at different temperatures, the peaks are labeled with the Miller indices of standard crystalline cuprite.

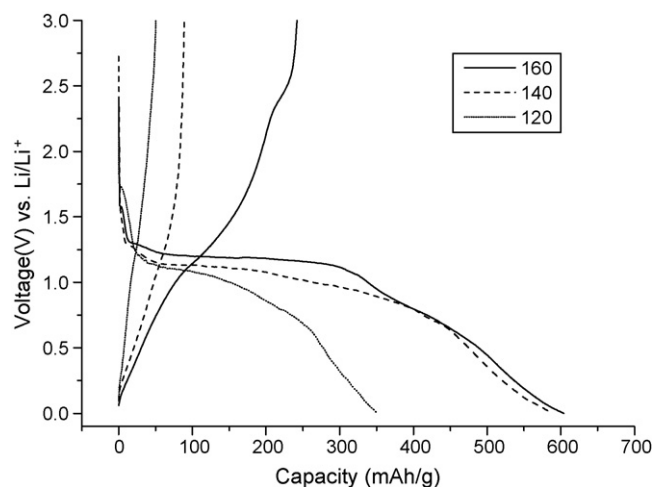
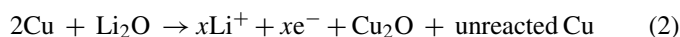


Fig. 4. Charge and discharge curves of Cu_2O samples prepared at different temperatures during the first cycle at a constant current density of 0.1 mA cm^{-2} in the voltage range 0–3 V.

process, the reaction in the voltage range from 2.0 to 3 V is described as



The capacity below 2.0 V during the charge process is supposed to be the deformation of a SEI-like organic layer.

During the discharge process, it appears that among morphology and degree of crystallinity, the latter mainly influences on the discharge performance of these samples.

It was proposed that in $\text{LiAl/LiCl} + \text{KCl}/\alpha\text{-Fe}_2\text{O}_3$ cells, the discharge reaction proceeds with insertion of lithium into and expulsion of iron from the starting Fe_2O_3 cubic close-packed phase to yield the final discharge products Li_2O and $\alpha\text{-Fe}$ [13]. Perhaps it is similar for the samples prepared at 120, 140, and 160°C since Cu_2O and Li_2O have a cubic-type structure with $a = 4.267$ and 4.614 \AA , respectively. It could be assumed that during the discharge process, Li atoms are driven to enter an oxygen framework and push the copper out to form Cu atoms and Li_2O [12], which is perhaps similar to the behavior of $\text{Cu}_{0.1}\text{V}_2\text{O}_5$ [14].

According to the above XRD data, the samples obtained at 140 and 160°C exhibit better crystallinity compared with the Cu_2O obtained at 120°C , leading to a better phase transformation between Cu_2O and Li_2O , resulting in a larger discharge capacity than that of the Cu_2O prepared at 120°C . Regarding the charge profile, we assume that the morphological differences among the three samples play an important role in their charging performance. Cu_2O is known to be a poor semiconductor. Large diameter of the particles and thick shell restrict the mobility of charge carriers and produce larger polarization [15]. Consequently, the reaction (2) proceeds to a less extent, leading to lower reversible capacity for the samples prepared at 120 and 140°C . In contrast, for the Cu_2O prepared at 160°C , the small particle size and thin shell benefit the diffusion of charge carriers, resulting in larger reversible capacity.

Further investigation of the electrochemical performance was done with cyclic voltammetry. Fig. 5 shows CVs of Cu_2O

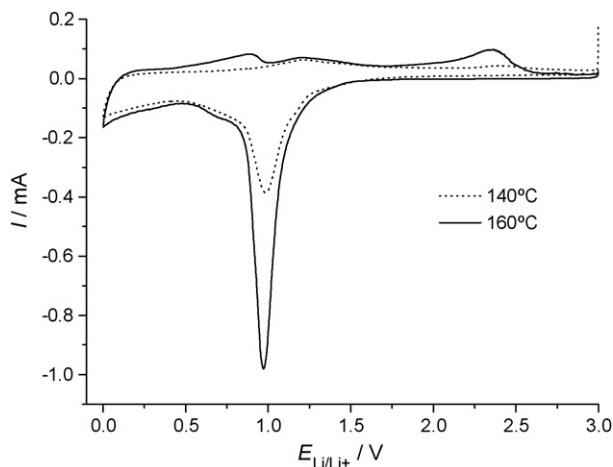


Fig. 5. Cyclic voltammograms of Cu_2O samples synthesized at 140 and 160 °C between 0 and 3 V at a scanning rate of 0.1 mV s^{-1} .

samples synthesized at 140 and 160 °C measured between 0 and 3 V at a scanning rate of 0.1 mV s^{-1} . For both samples prepared at 140 and 160 °C, a well-defined peak ranging from 1.3 to 0.8 V and a broad peak in the range of 0.3–0 V are observed during the cathodic process. The former sharp and strong peak can be ascribed to the reduction of Cu_2O to Cu matrix and formation of Li_2O , the latter broad and weak peak from 0.3 to 0 V is due to the formation of a solid electrolyte interface (SEI) like an organic layer [12]. During the anodic polarization process, besides the peak ranging from 2.0 to 2.7 V, which can be ascribed to conversion of Cu back to Cu_2O and deformation of Li_2O , there are two further peaks in the range of 0.8–1.0 and 1.2–1.5 V. These two peaks are attributed to the deformation of the SEI-like organic layer and its partial dissolution [12]. However, in the CV of the Cu_2O sample prepared at 140 °C, the currents of both the cathodic and anodic peaks are much smaller than those of the samples prepared at 160 °C. This is most likely due to morphological differences between the two samples. The thinner shell and smaller diameter of core-shell structured Cu_2O particles prepared at 160 °C are superior in the mobility of charge carrier, giving rise to larger peak current compared to that of the Cu_2O prepared at 140 °C.

4. Conclusions

In summary, Cu_2O samples with different morphologies have been synthesized with a polyol process at different temperatures.

The samples prepared at 160 and 140 °C present a core-shell structure and better crystallinity. Different morphologies and degree of crystallinity play an important role in determining the electrochemical performance of Cu_2O samples. Better crystallinity leads to larger discharge capacity, and smaller particle size with thinner shell result in higher coulombic efficiency and larger reversible capacity.

Acknowledgments

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