Journal of Power Sources 312 (2016) 199–206

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

# Morphology- and facet-controlled synthesis of CuO micro/nanomaterials and analysis of their lithium ion storage properties

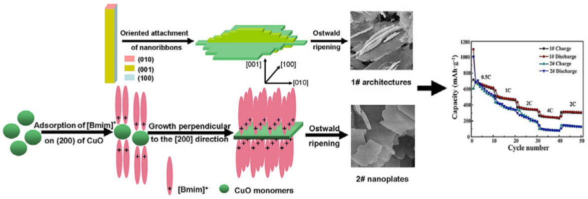
Xiaodi Liu [a, *], Guangyin Liu [a], Lijuan Wang [a], Yinping Li [a], Yupei Ma [a], Jianmin Ma [b]

[a] College of Chemistry and Pharmaceutical Engineering, Nanyang Normal University, Nanyang, Henan, China
[b] State Key Laboratory of Chemo/Biosensing and Chemometrics, Hunan University, Changsha, Hunan, China

## HIGHLIGHTS

- CuO architectures and CuO nanoplates with different exposed facet are synthesized.
- Ionic liquid [Bmim]Cl serves as template for the controlled growth of CuO nanoplates.
- CuO architectures have better electrochemical property than CuO nanoplates.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

*Article history:*
Received 9 October 2015
Received in revised form
30 January 2016
Accepted 15 February 2016

*Keywords:*
CuO
Hierarchical architectures
Nanoplates
Hydrothermal method
Lithium-ion battery

## ABSTRACT

Hierarchical CuO architectures and monodisperse CuO nanoplates are synthesized *via* a hydrothermal method with the assistance of ionic liquid 1-butyl-3-methylimidazolium chloride ([Bmim]Cl). The products are characterized by XRD, SEM, TEM, HRTEM, BET, and XPS, and the results indicate that the CuO architectures are composed of nanosheets with exposed (001) facets and the CuO nanoplates are single crystals enclosed by (200) facets. More specially, it is found that [Bmim]Cl serves as an effective template for the synthesis of CuO nanoplates by adsorbing on the (200) planes of monoclinic CuO. When evaluated as anode materials for lithium-ion batteries, CuO architectures possess higher discharge capacity, better cycling stability, and better rate capability than CuO nanoplates. The initial discharge capacity of CuO architectures is 1096 mAh $g^{-1}$ at a rate of 0.5 C, whereas CuO nanoplates exhibit a lower capacity of 878.4 mAh $g^{-1}$. Moreover, after 50 cycles, CuO architectures and CuO nanoplates can deliver discharge capacities of 465.6 and 281.6 mAh $g^{-1}$, respectively.

## 1. Introduction

More recently, it has been demonstrated that the physical and chemical properties of micro/nanomaterials are closely related to their sizes, morphologies and exposed facets, so the rational design and fabrication of micro/nanomaterials with distinct morphologies and facets are important for many technological applications, such as lithium-ion batteries (LIBs), gas sensor, and photocatalysis [1–3]. Thereinto, LIBs have made great contribution to many fields including portable electronic devices, intelligent grid, and electric vehicles [4,5]; hence much research effort has focused on the controlled synthesis of micro/nanostructured electrode materials for LIBs to improve their electrochemical performance, particularly with regard to high gravimetric capacity, high rate capability, and long cycle life [6]. Until now, a variety of transition metal oxides (TMOs) have been found to be potential substitutions for graphite as anode materials for LIBs because of their high theoretic capacity (450–1500 mA h $g^{-1}$) [7]. Recently, TMOs micro/nanomaterials

---

* Corresponding author.
*E-mail address:* liuxiaodiny@126.com (X. Liu).

http://dx.doi.org/10.1016/j.jpowsour.2016.02.048

with various morphologies have been prepared and the relationships between shape and property have been deeply studied [8–10]. Nevertheless, the facet-controlled synthesis of TMOs and their facet-dependent electrochemical properties have been rarely investigated and only a few successfully examples (*e.g.*, $TiO_2$, $Co_3O_4$, and $Fe_2O_3$) have been reported [11–14]. For instance, the diffusion of $Li^+$ ions in the anatase framework is more efficient along the *c* axis than in the *ab* plane, so $TiO_2$ microspheres assembled by nanosheets with exposed (001) facet have high Coulombic efficiency for lithium extraction and good capacity retention [13]. Li and co-workers have confirmed that the (111) plane of $Co_3O_4$ contains more $Co^{2+}$ than other planes, which is more beneficial to $Li^+$ transportation; therefore, $Co_3O_4$ octahedron with (111) plane shows excellent rate capability [14]. In these regards, there remains an urgent need to explore facile and effective methods for accurately tuning the crystallographic facets and morphologies of TMOs anode materials.

CuO, as an important *3d* transition metal oxide, has been considered as a promising anode candidate for LIBs owing to its non-toxicity, low cost, chemical stability, and high theoretical capacity (674 mAh $g^{-1}$) [15]. So far, various CuO micro/nanomaterials have been developed to obtain high-performance anodes [4,16–20]. However, to the best of knowledge, the research on the role of crystal planes of CuO in the electrochemical property has not been established. Therefore, there is still much room for the development of CuO with controllable facets and shapes. Furthermore, the comprehension on the structure-performance relationship of CuO may offer new opportunity for constructing CuO materials with novel structures and exciting properties.

Based on Gibbs-Wulff's theory, the equilibrium shape of a crystal is the shape which can minimize its surface energy. In the crystal growth process, additives can preferentially adsorb on a certain facet and then change the relative order of surface energy, which would hinder the crystal growth along the normal direction and lead to the formation of non-equilibrium Wulff constructions. Hence, according to the above principle, organic and inorganic templates have been employed to tune the shape and structure of the micro/nanomaterials [21,22]. Ionic liquids (ILs), consisting of organic cations and inorganic anions, have attracted increasing attention in the inorganic synthesis owing to their unique physico-chemical properties [23]. Moreover, their properties can be tailored by judiciously changing the cations and anions [24]. More particularly, crystal growth in ILs offers a wide range of possible micro/nanostructures, which are difficult to achieve by other synthetic routes. In the previous reported researches, ILs have served as templates for the synthesis of inorganic micro/nanomaterials [25–28]. Inspired by these potentials, we consider that ILs can be used as effective templates to prepare nanoscale CuO with special structures.

Herein, CuO architectures and CuO nanoplates with different exposed facets are fabricated *via* a hydrothermal method with the assistance of IL 1-butyl-3-methylimidazolium chloride ([Bmim]Cl). The potential formation mechanisms of CuO architectures and CuO nanoplates are discussed in detail. Furthermore, we compare the lithium storage performance of the two samples to investigate the relationship between property and structure.

## 2. Experimental section

### 2.1. Chemicals

All chemicals are purchased from Comio Chemical Reagent Co., Ltd. (Tianjin, China), and they are analytical reagent grade and are used without further purification. Based on the literature [29], 1-chlorobutane and 1-methylimidazole with the molar ratio of 1:1 are added into a round bottomed flask fitted with a reflux condenser; then the reactants are refluxed at 70 °C for 48 h with stirring. The product is washed with acetone, evaporated on a rotary evaporator, and then dried in a vacuum oven at 70 °C for 48 h. Finally, [Bmim]Cl is prepared.

### 2.2. Synthesis of CuO architectures and CuO nanoplates

#### 2.2.1. CuO architectures

In the synthesis, 0.125 g $CuSO_4 \cdot 5H_2O$ is dissolved into deionized water (5 mL) to form a clear solution and aged 10 min, and then 5 mL NaOH solution (0.4 M) is added into the $CuSO_4$ solution. Subsequently, the mixture is stirred for 20 min, transferred into a Teflon-lined stainless steel autoclave (20 mL), and treated hydrothermally at 140 °C for 10 h. After the autoclave is cooled to room temperature, the precipitate is collected by centrifugation, washed with deionized water and anhydrous ethanol, and then dried in a vacuum oven at 50 °C for 8 h.

#### 2.2.2. CuO nanoplates

The same procedure as for the synthesis of CuO architectures is used for the fabrication of CuO nanoplates, except that $CuSO_4 \cdot 5H_2O$ (0.125 g) and [Bmim]Cl (0.4 g) are dissolved into 5 mL deionized water to form a solution and aged 10 min to make $Cu^{2+}$ and $SO_4^{2-}$ homogeneously diffuse in the solution.

### 2.3. Instruments and characterizations

The phase compositions of the products are characterized by X-ray diffraction (XRD) on a Rigaku D/max 2500V/PC X-ray diffractometer with Cu K$\alpha$ radiation ($\lambda = 1.54056$ Å) at a scanning rate of $0.05^\circ \cdot s^{-1}$. The transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) micrographs are taken with a JEM-2100 transmission electron microscopy, which are operated at an accelerating voltage of 100 kV and 200 kV, respectively. The shapes of the products are examined with a JSM 6700F scanning electron microscopy (SEM). X-ray photoelectron spectra (XPS) of the samples are carried out by a Thermo ESCALAB 250XI multifunctional imaging electron spectrometer, using Al K$\alpha$ radiation as the exciting source, and the data are calibrated by setting the adventitious C 1s peak at a fixed value of 284.5 eV and analyzed using the XPSPEAK41 software. The special surface areas of the samples are performed through measuring the $N_2$ adsorption-desorption isotherms at 77 K on a Beishide 3H-2000PS2 surface area analyzer, using the Brunauer-Emmett-Teller (BET) theory.

### 2.4. Electrochemical measurements

The Li storage performance is investigated in Li test cells for CuO architectures and CuO nanoplates. The anode electrodes are prepared by mixing 70 wt% active materials (CuO), 20 wt% acetylene black, and 10 wt% binder (polyvinylidene fluoride, PVDF) and dispersing the mixture in *N*-methyl-2-pyrrolidinone (NMP). After uniformly coating the above slurry on Cu foils, the electrodes are then dried in a vacuum oven at 120 °C for 10 h to remove the solvent. The electrodes are cut into disks of 12 mm in diameter, pressed at 298 K and 4 Mpa, and then assembled into cells in an Argon-filled glove box. Lithium is used as counter and reference electrode. The electrolyte is 1 M $LiPF_6$ dissolved in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) with the volume ratio of 1:1. Finally, the cells are charged and discharged on a LAND-CT2001 battery testing system (Wuhan, China) in the voltage range of 0.01–3.0 V (*vs.* $Li^+/Li$) under different current densities.