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Boosted electrochemistry properties of $Cu_4[(OH)_{0.29}Cl_{0.71}](OH)_6$ hexagonal prisms by 3D-cage atomic configuration of (100) facet

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ABSTRACT

The $Cu_4[(OH)_{0.29}Cl_{0.71}](OH)_6$ hexagonal prisms, nanoplates and nanosheets are prepared by a simple hydrothermal method, and we have mainly investigated their electrochemistry properties. At 31.25, 62.5, 125, 250 and 500 mAg^{-1}, the discharge capacitances of hexagonal prisms (S0) electrode are 1186, 1023, 969, 934 and 918 mFg^{-1}, respectively; whereas 547, 508, 469, 438 and 375 mFg^{-1} for hexagonal nanosheets (S10), respectively. The capacitance of 3–8 μm-long hexagonal prisms (0.25 m^2g^{-1}) is 2 times higher than that of 50–100 nm-thick hexagonal nanosheets (3.54 m^2g^{-1}), which is obviously beyond our imagination. The high capacitance of the former sample has been mainly attributed to the atom configuration of {100} facets and the high electrical conductivity. Compared with the hexagonal tunnel atom configuration of {001} facets, the three-dimensional (3D) cage atom configuration in {100} facets favors for the charge storage, thus leading to a higher capacitance of hexagonal prisms, which has rarely been reported yet. Further, the hexagonal prisms have a higher electrical conductivity than nanoplates and nanosheets, suggesting that the one-dimensional (1D) microstructure is beneficial to the electron transfer. This work enlightens us that the electrochemistry properties of materials can be improved by the exposed facets with unique atom configuration.

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1. Introduction

Since traditional fossil fuels cannot meet the increasing demand for energy now [1], it is important to develop the sustainable, renewable resources [2,3]. Among the alternative energy technologies, the super capacitors are have attracted increasing attention [4,5]. According to charge storage mechanism, super capacitors are usually classified into electrical double layer capacitors (EDLC) and pseudo-capacitors. The former is based on ion adsorption and accumulation at the electrode/electrolyte interface, which is mainly limited by the available electrochemical surface and electrical conductivity of materials [6]. The latter is based on the oxidation-reduction reactions. Nevertheless, the energy density of super capacitor is usually lower than that of battery [7,8]. Hence, it is still a big challenge to develop a high-energy-density electrode material for practical applications.

Up to now, numerous electrode materials, including graphene [9,10], and metals oxides [11–15], copper and copper-containing materials [16–19], *etc.* have been developed. Among copper-containing materials, chlorocuprates are often used as the absorbent or the sacrificial template to prepare the other catalysts [20–22]. Nevertheless, their electrochemical properties have rarely studied before. Herein, we have mainly investigated the electrochemistry properties of $Cu_4[(OH)_{0.29}Cl_{0.71}](OH)_6$ as the super capacitor electrode, and mainly revealed the correlation of electrochemistry properties with the crystal facets exposed.

In this work, the $Cu_4[(OH)_{0.29}Cl_{0.71}](OH)_6$ samples were prepared by a simple hydrothermal method; and we have also investigated the effects of the F and CTAB concentrations, hydrothermal temperature and time on the samples. The samples were characterized by X-ray powder polycrystalline diffraction (XRD), scanning electron microscope (SEM), high-resolution electron transmission microscope (HRTEM) with electron diffraction (ED), and nitrogen sorption isotherms. Moreover, the correlation of electrochemistry properties with the crystal facets exposed was mainly revealed. This contribution demonstrates that the electro-

Table 1
Synthesis parameters of the samples.

Sample	CTAB (mmol)	NaF (molL^{-1})	Temperature (°C)	Time (h)
S0	0	0.16	100	24
S1	4	0	100	24
S2	4	0.16	100	24
S3	4	0.64	100	24
S4	4	4	100	24
S5	4	8	100	24
S6	4	16	100	24
S7	4	32	100	24
S8	4	32	100	6
S9	4	32	50	24
S10	4	32	50	6

chemistry properties can be improved by the crystal facets exposed of material, which has rarely been reported yet.

2. Experimental

2.1. Synthesis of $Cu_4[(OH)_{0.29}Cl_{0.71}](OH)_6$

All reagents were of analytical grade, purchased from Beijing Chemical Reagents Industrial Company of China, and were used without further purification.

Typically, 4 mmol $CuCl_2$ and 25 mL of 0.24 M NaOH solution were mixed together under stirring at room temperature. After stirring for 10 min, 4 mmol CTAB and the measured amount of NaF were added to the above solution. After stirring for another 10 min, the mixture was transferred into a Teflon-lined stainless steel autoclave and kept at a certain temperature for a certain time. When the reaction was completed, the autoclave was cooled to room temperature naturally. The blue product was harvested by centrifugation, washed with deionized water for several times, and dried overnight at 60 °C for 6 h. The detailed preparation conditions were provided in Table 1. Except for S0, the other samples were all prepared in the presence of 4 mmol CTAB, S1 and S3–S7 were prepared at different F concentrations, and S8–S10 were prepared at different reaction temperatures and times.

2.2. Characterization

The crystal phases of the samples were characterized by X-ray diffraction (XRD, RigakuD/max-2550VB) with graphite monochromatized Cu K_α radiation ($\lambda = 0.154$ nm), operating at 40 kV and 50 mA. The XRD patterns were obtained in the range of 10–80° (2θ) at a scanning rate of 7° min^{-1}. The particle morphology was characterized by scanning electron microscope (SEM, Hitachi, SU-1510) using an accelerating voltage of 15 kV. The fine surface structures of the samples were characterized by high-resolution transmission electron microscopy (HRTEM, JEOLJEM-2100F) equipped with an electron diffraction (SAED) attachment with an acceleration voltage

of 200 kV. Nitrogen sorption isotherms were obtained at 77 K using the Autosorb-iQ physicoadsorption apparatus (Quantachrome). Surface area was calculated by the Brunauer-Emmett-Teller (BET) method.

2.3. Electrochemical measurements

All the electrochemical measurements were carried out on a CHI 660D electrochemical Working Station at room temperature. For a standard three-electrode cell, a 0.5 M Na_2SO_4 aqueous solution was used as the electrolyte. Nickel was used as the current collector of working electrode (with an area of 1 cm^2), Pt wire (diameter: 0.1 cm, length: 4 cm) and Hg/HgO (S.C.E) electrodes were used as the counter and reference electrodes, respectively. To fabricate the working electrode, 80 wt% of active materials ($Cu_4[(OH)_{0.29}Cl_{0.71}](OH)_6$), 10 wt% of acetylene black (conducting agent) and 10 wt% of polyvinylidene fluoride (binder) were dispersed in 1-methyl-2-pyrrolidinone to form a homogeneous slurry. Then the slurry was dotted on the nickel and dried for 24 h at room temperature. The mass of active material ($Cu_4[(OH)_{0.29}Cl_{0.71}](OH)_6$) on the nickel is 0.08 g. Cyclic voltammetry (CV) and chronopotentiometry (CP) were both conducted in a potential range of 0–0.8 V (vs. S.C.E). Electrochemical impedance spectroscopy (EIS) was performed from 0.1 Hz to 100 KHz at an open circuit potential and an alternating current (AC) voltage amplitude of 5 mV. Areal capacitances were calculated using the following equation.

$$Csp = I·t/\Delta V·m$$

where I is the constant discharge current, t is the discharging time, ΔV is the voltage drop upon discharging (excluding the IR drop), m is the mass of the active material.

3. Results and discussion

3.1. Formation of hexagonal $Cu_4[(OH)_{0.29}Cl_{0.71}](OH)_6$

First, we have investigated the effect of CTAB on the sample. Typically, the S0 and S2 samples (Table 1) are prepared without and with adding CTAB in the presence of NaF, respectively. Fig. 1(a) shows that all the diffraction peaks of the S0 and S2 samples can be well indexed to standard card ICSD #86-0899, and no impurities peaks can be detected in the XRD patterns, confirming the formation of phase-pure $Cu_4[(OH)_{0.29}Cl_{0.71}](OH)_6$. Further, Fig. 1(b,c) shows that, the 3–8 μm long hexagonal prisms have formed without adding CTAB (S0); when CTAB is added, however, the hexagonal prisms become irregular and shorter, which are 0.5–1.5 μm long (S2). It is obvious that the addition of CTAB has reduced the length of hexagonal prisms.
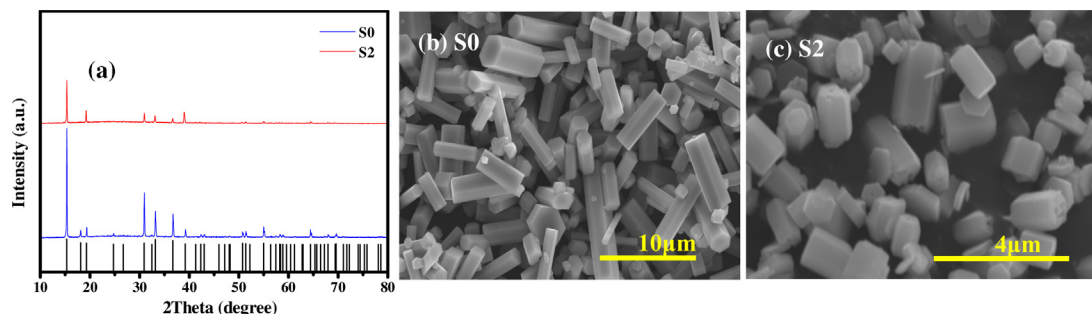

Fig. 1. (a) XRD patterns and (b) SEM images of the as-prepared samples: S0, without adding CTAB; (c) S2, with adding CTAB. The preparation details are given in Table 1.