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Effect of Precursor on the Morphology and Supercapacitor Performance of CuCo₂O₄

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Two CuCo₂O₄ spinel crystals with different morphologies were successfully synthesized by one step hydrothermal method and used as active electrode materials for supercapacitors. A chrysanthemumlike CuCo₂O₄ crystal (CuCo₂O₄-C) was obtained by using cobalt chloride and copper chloride as the raw materials, and a rose-like CuCo₂O₄ crystal (CuCo₂O₄-N) was prepared by using cobalt nitrate and copper nitrate. The structural analysis results indicated that CuCo₂O₄-C has a more open-framework structure. The following electrochemical tests showed that the CuCo₂O₄-C electrode exhibited a better supercapacitive performance than that of CuCo₂O₄-N in 6 mol L⁻¹ KOH solution. The specific capacitance of CuCo₂O₄-C was 335.8 F g⁻¹ at a current density of 0.5 A g⁻¹, however, the capacitance of CuCo₂O₄-N was only 235.3 F g⁻¹ under the same conditions. Furthermore, at a current density of 3 A g⁻¹, the capacitance retention of the CuCo₂O₄-N electrode remained at 85% after 2000 cycles, whereas the retention of the CuCo₂O₄-N electrode was only 67%. The peculiar structure of chrysanthemum-like CuCo₂O₄-C, which affords a highly porous structure and an enhanced specific surface area, helps to explain these results.

Keywords: CuCo₂O₄, Chrysanthemum-like, Rose-like, Supercapacitor performance

1. INTRODUCTION

Due to energy exhaustion and serious global warming, the development of alternative energy storage and conversion systems cannot wait [1-3]. Due to their many advantages such as minimal environmental pollution, high cycle efficiency, wide operating temperature range, and high power density, supercapacitors, also known as ultracapacitors or electrochemical capacitors, have become a research hotspot for energy storage devices in the 21st century. The electrode materials play an important role in the performance of supercapacitors. According to the energy storage mechanism

difference, supercapacitors can be divided into two categories: electrochemical double-layer capacitor (EDLC) and pseudocapacitor. The energy storage of an EDLC is caused by an accumulation of charge in the electrode/electrolyte interface [4, 5], while a pseudocapacitor is based on the Faraday redox reactions at electrochemically active sites [6, 7]. Compared to EDLCs, pseudocapacitors potentially have higher energy densities and specific capacitances owing to the reversible redox processes. Therefore, research efforts on the electrode materials of pseudocapacitors should lead to improvement in the performance of supercapacitors.

Owing to their ultrahigh theoretical specific capacitance, many transition metal oxides (TMOs) used as pseudocapacitor electrodes have been intensively studied, for instance, Co₃O₄, MnO₂, RuO₂, and NiO. Recently, metal composite oxides have been widely reported as one of the prime components of supercapacitor electrodes. Because metal composite oxides have cations with multiple valences, used as electrode materials, leads to additional electrochemically active sites for redox reactions and improves the supercapacitive performance [8, 9]. Among the metal composite oxides, spinel-type metal composite oxides AB₂O₄ have been examined. The element A denotes divalent metallic cations, such as Cu²⁺, Mg²⁺ Zn²⁺, and B refers trivalent metallic cations, such as Fe³⁺ and Co³⁺. Spinel-type metal composite oxides are intriguing materials due to their better chemical stability and reactivity than that of mono metal oxides. Cobalt-based composite metal oxides, MCo₂O₄ (M=Ni, Cu, Zn, Mn, Mg, Cd, etc.) are especially promising materials and have been extensively studied [10-13].

CuCo₂O₄ is a promising material for use in psedocapacitors [14], lithium ion batteries [15], and electrocatalyst for oxygen evolution [16], because this material incorporates multiple oxidation states as well as higher conductivity than that of copper oxide and cobalt oxide [17]. Hydrothermal method is considered an excellent method to synthesize the electrode materials due to the ease of controlling the size and morphology of the crystals via control of the reaction conditions. Various morphologies of copper cobalt oxide have been extensively researched. Liu et al synthesized CuCo₂O₄ nanosheets using a hydrothermal method [18]. Yuan et al prepared CuCo₂O₄ concave polyhedra coated by carbon with the assistance of a metal organic framework [19]. Kang et al synthesized porous CuCo₂O₄ nanocubes by a microwave-assisted solvothermal reaction [20]. These micro-nanostructured materials have been demonstrated to be a preeminent candidates for efficient energy storage and conversion due to their special structures that can provide large surface areas and short ionic diffusion distances [18-21].

Based on the above considerations, two $CuCo_2O_4$ crystals with different morphologies , chrysanthemum-like and rose-like $CuCo_2O_4$ crystals, were prepared by controlling type of the raw materials used during the synthesis. We also investigated the electrochemical performance of the $CuCo_2O_4$ crystals as electrodes for supercapacitors. The superior performance of the chrysanthemum-like $CuCo_2O_4$ crystals was ascribed to the unusual structure containing more abundant channels and a higher specific surface area.

2. EXPERIMENTAL

2.1. Materials preparation

The CuCo₂O₄ crystals were synthesized as follows. In a typical experiment, 4 mM CoCl₂· $6H_2O$ and 2 mM CuCl₂· $2H_2O$ were combined in 60 mL of deionized water and stirred for 30 min.

2.2 Structural characterization

The powder X-ray diffraction (XRD) measurements of the crystals were carried out with a Smart Lab X' pert diffractometer with Cu K α radiation at 45 kV and 40 mA with a step of 4° min⁻¹. The morphology was characterized by scanning electron microscopy (SEM) using a Zeiss SIGMA. The X-ray photoelectron spectroscopy (XPS) results were performed on a Thermo Scientific ESCALAB 250Xi X-ray photoelectron spectrometer. Nitrogen (N₂) adsorption/desorption curves were obtained using a Quantachrome NOVA 2200e.

2.3 Working electrode preparation

The working electrode was formulated by a coating method. The active material (70 wt. %), carbon black (20 wt. %) and polyvinylidene fluoride (10 wt. %) were mixed well and evenly grind. A few drops of N-methyl pyrrolidone (NMP) were added to the mixture and stirred to form a mushy mixture. The mass loading of active materials was 10 mg. Then the mixture was overlaid on a Ni foil $(2 \times 1 \text{ cm}^2 \text{ in square shape})$ used as a current collector. Finally, the prepared electrode was dried overnight at 60 °C prior to use.

2.4 Electrochemical performance evaluation

Electrochemical tests were carried out with an RST 5200F electrochemical workstation in 6 M KOH in a three-electrode setup. The as-prepared electrode was used as the working electrode. The standard Hg/HgO electrode was used as the reference electrode, with a platinum plate electrode as the counter electrode. When the working electrode potential changed, the corresponding response current changed and formed a cyclic voltammetry (CV) curve. The voltage range was from -0.2 to 0.6 V in our tests. We obtained the galvanostatic charge-discharge curves (GCD) at different current densities and a voltage range from -0.2 to 0.55 V. To minimize the error, each group of tests was repeated five times to obtain an averaged value. Electrochemical impedance spectroscopy (EIS) tests were performed in a frequency range of 0.01 to 100 kHz with an AC voltage amplitude of 7 mV.

3. RESULTS AND DISCUSSION

3.1. Characterization



Figure 1. XRD patterns of CuCo₂O₄-N and CuCo₂O₄-C.

The crystalline structures of the two samples were characterized by XRD and are shown in Figure 1. The diffraction peaks for the CuCo₂O₄-N and CuCo₂O₄-C samples occurred at 2 θ values of 19.1, 31.4, 36.9, 38.9, 45.1, 56.0, 59.6 and 65.7°, which can be indexed as the (111), (220), (311), (222), (400), (422), (511) and (440) crystal planes of spinel CuCo₂O₄, respectively (JCPDS card No. 01-1155) [22]. There was no impurities or other crystal phases in the typical pattern. Clearly, the diffraction peaks of CuCo₂O₄-N and CuCo₂O₄-C are quite similar, which illustrates that the type of precursor does not affect the crystalline phase or crystallinity of the CuCo₂O₄.



Figure 2. SEM images of rose-like CuCo₂O₄-N (a-c) and chrysanthemum-like CuCo₂O₄-C (d-f) samples.

Figure 2 shows the SEM images of the as-synthesized CuCo₂O₄-N and CuCo₂O₄-C samples at different magnifications. The uniform rose-like CuCo₂O₄-N sample (Figure 2, a-c) was formed by a few regularly intercalated flakes. The average thickness of the flakes was approximately 50 nm. The chrysanthemum-like CuCo₂O₄-C sample (Figure 2, d-f) was composed of a large number of needle-shaped nanorods, densely gathered from the center. The nanoneedles were 4-5 μ m long with a diameter of 50 nm, thus, CuCo₂O₄-C possessed a highly porous structures with more open spaces. Increasing the specific area may improve the special capacitance. It is due to the different precursor, leading to a large difference in the morphology of the CuCo₂O₄ samples, which in turn may affect the electrochemical properties of the CuCo₂O₄ electrode.

The porosity was confirmed by N₂ adsorption-desorption measurements. As shown in Figure 3, the two curves are characteristic of type IV with a type H3 hysteresis loop in the 0.5-0.9 P/P₀ range. According to the calculations based on BJH theories, the CuCo₂O₄-C sample gave rise to a relatively high BET specific surface area of 24.18 m² g⁻¹ and a pore volume of 0.073 cm³ g⁻¹. However, the specific surface area of CuCo₂O₄-N only reached 8.51 m² g⁻¹, a decrease of two-third compared to CuCo₂O₄-C. Considering that a highly porous structure is beneficial to the diffusion of ions and

electrode-electrolyte contacts in an electrochemical reaction, the chrysanthemum-like CuCo₂O₄-C may have a superior electrochemical performance than that of CuCo₂O₄-N with rose-like morphology. This result is also consistent with SEM analysis.

Figure 3. N₂ absorption-desorption isotherms of CuCo₂O₄-N and CuCo₂O₄-C.

Figure 4. XPS spectra of CuCo₂O₄ samples: (a) full survey spectra, (b) Cu 2p, (c) Co 2p, (d) O 1s.

In addition, the distribution of elements present and oxidation states of the $CuCo_2O_4$ samples were characterized by XPS. As shown in Figure 4a, the full survey scan spectrum indicated the presence of C, Co, Cu and O in the sample, and that C came from conductive substrates. No other impurities were observed. The Cu 2p spectrum is shown in Figure 4b. Two peaks centered at 952.1 and 932.3 eV are well fitted with 2p 1/2 and 2p 3/2. In addition, the peak at approximately 942.2 eV was assigned to the typical satellite (identified as "Sat.") of Cu^{2+} . In Figure 4c, the spectrum showed a main peak at 797.2 eV and a shoulder peak at 781.4 eV, which corresponded to Co 2p 1/2 and Co 2p 3/2, respectively. The accompanying satellite peaks at approximately 802.5 and 786.2 eV are indicative of the presence of Co^{2+} and Co^{3+} . These results show that the synthesized $CuCo_2O_4$ samples are composed of Cu^+ , Cu^{2+} , Co^{2+} and Co^{3+} , in good agreement with literature results for $CuCo_2O_4$ [16, 23, 24]. The high-resolution spectrum for the O 1s region (Figure 4d) shows two oxygen contributions, O1 and O2. Specifically, the O1 peak at 527.8 eV is typical of Cu-O and Co-O bonds. The O2 centered at 531.3 eV corresponds to a high amounts of defectives sites with minimum oxygen co-ordination in the micro- and nanostructured materials [25-27].

3.2 Electrochemical performance analysis

The electrochemical performance of the rose-like $CuCo_2O_4$ -N and chrysanthemum-like $CuCo_2O_4$ -C electrodes were all performed in a three-electrode cell containing an aqueous 6 M KOH electrolyte. Figure 5 (a and b) displays the typical CV profiles of the $CuCo_2O_4$ -C and $CuCo_2O_4$ -N electrodes in the potential range from -0.2 to 0.6 V at different scan rates (5 to 100 mV s⁻¹). The CV curves reveal analogous cathodic and anodic peaks, indicating the fast redox reaction behavior of $CuCo_2O_4$ -N and $CuCo_2O_4$ -C in 6 M KOH, which is attributed to a superior pseudocapacitive feature [28, 29]. The processes are believed to be based on the following equations:

 $\begin{aligned} CuCo_2O_4 + 2H_2O + e^- &\longleftrightarrow 2CoOOH + CuOH + OH^- \\ CoOOH + OH^- &\longleftrightarrow CoO_2 + H_2O + e^- \\ CuOH + OH^- &\longleftrightarrow Cu(OH)_2 + e^- \end{aligned}$

As the scan rate increased from 5 to 100 mV s⁻¹, the current density for both the rose-like $CuCo_2O_4$ -N and chrysanthemum-like $CuCo_2O_4$ -C also increased, verifying that the materials both have good ion and electron conductivity, even at high scan rates.

Figure 5. Electrochemical tests in 6 mol L⁻¹ KOH electrolyte: CV curves of CuCo₂O₄-C (a) and CuCo₂O₄-N (b) with scan rates ranging from 5 to 100 mV s⁻¹; CV curves of CuCo₂O₄-C and CuCo₂O₄-N at the scan rate of 50 mV s⁻¹(c); GCD curves of CuCo₂O₄-C (d) and CuCo₂O₄-N (e) with current densities varying from 1 to 10 A g⁻¹; GCD curves of CuCo₂O₄-C and CuCo₂O₄-N at a current density of 1.5 A g⁻¹ (f).

However, compared to the CuCo₂O₄-N electrode, the CV curves of the CuCo₂O₄-C electrode obviously expanded when the scan rate was 50 mV s⁻¹ (Figure 5c). Figure 5c clearly shows that the chrysanthemum-like CuCo₂O₄-C electrode processes a larger capacitance, which results from its highly porous structure and enhanced specific surface area.

The electrochemical performance of the synthesized electrodes were further evaluated by GCD tests. Figure 5 (d and e) shows the charge and discharge curves of the CuCo₂O₄-C and CuCo₂O₄-N electrodes at current densities from 1 to 10 A g⁻¹. The curves of the two plots both display quite symmetrical features, implying high charge-discharge columbic efficiency, wonderful reversibility of redox reactions and outstanding rate capability. For comparison, the GCD curves at 1.5 A g⁻¹ of the CuCo₂O₄-C and CuCo₂O₄-N electrodes were carried out (Figure 5f). Evidently, the much longer charge-discharge time of the chrysanthemum-like CuCo₂O₄-C electrode confirms its higher charge storage capacity, consistent with the CV experimental results.

Figure 6. (a) Specific capacitances of CuCo₂O₄-C and CuCo₂O₄-N at different current densities; (b) cycling stability of CuCo₂O₄-C and CuCo₂O₄-N at a current density of 3 A g⁻¹; (c) EIS curves of CuCo₂O₄-N and CuCo₂O₄-C.

The specific capacitance of the electrodes can also be calculated from GCD curves using the following equation [30]:

$$C_m = \frac{I \times \Delta t}{m \times \Delta V}$$

where m is the mass of the electrode active material (g), ΔV is the potential window (V), Δt is the discharge time (s), and I is the constant discharge current (A). Figure 6a shows the relationship of the specific capacitance and current density of the two electrodes. The CuCo₂O₄-C electrode had the specific capacitances of 335.8, 313.6, 294.8, 287.1 and 239.5 F g⁻¹ at current densities of 0.5, 2, 5, 8 and 15 A g⁻¹, respectively. These results were much higher than that of CuCo₂O₄-N, whose capacitance values were just 235.3, 215.2, 200.0, 191.3 and 184.3 F g⁻¹ at current densities of 0.5, 2, 5, 8 and 15 A g⁻¹. Furthermore, the capacitance retention of the CuCo₂O₄-C electrode reached 85.5% (335.8~287.1 F g⁻¹) from 0.5 to 8 A g⁻¹, whereas CuCo₂O₄-N merely remained at 81.3% (235.3~191.3 F g⁻¹) of the highest value in the same conditions. These results again demonstrate that the specific capacitance and rate capability of the CuCo₂O₄-C electrode surpass those of CuCo₂O₄-N.

In the process of fast charge/discharge, high current density is particularly significant for supercapacitor performance testing. Thus, we further investigated $CuCo_2O_4$ electrodes at a relatively

high current density of 3 A g^{-1} (Figure 6b). As the figure shows the cycling performance of the CuCo₂O₄ electrodes at a constant current density of 3 A g^{-1} . As figure shows, the specific capacitance of CuCo₂O₄-C electrode remains 85% of the original value after 2000 cycles, while the CuCo₂O₄-N electrode retained only 67% capacitance after the same number of cycles, revealing that the CuCo₂O₄-C electrode has better cycling stability for long cycle life applications.

Finally, EIS was measured to explain the electrochemical behavior of the CuCo₂O₄-N and CuCo₂O₄-C electrodes, the corresponding impedance Nyquist plots are shown in Figure 6c. In the low-frequency range, the sloped line is related to the Warburg impedance [31]. The CuCo₂O₄-C electrode showed a more ideal straight line than that of the CuCo₂O₄-N electrode, suggesting its more efficient ion diffusion and electron transfer. In the high-frequency area, the semicircle on the real axis corresponds to the equivalent series resistance (R_s), and its diameter represents the charge-transfer resistance (R_{ct}). From Figure 6c, the CuCo₂O₄-C electrode processed the lower R_s and R_{ct} values.

In summary, the chrysanthemum-like structure of $CuCo_2O_4$ -C electrode displayed higher specific capacitance, better cycling stability and lower charge-transfer resistance than did the rose-like structured $CuCo_2O_4$ -N electrode.

Materials	Structure	Specific current	Specific capacity	Ref.
CuCo ₂ O ₄	Nanoparticles	5 A g ⁻¹ 3 M KOH	175 F g ⁻¹	[28]
$CuCo_2O_4$	Nanowires	2 A g ⁻¹ 3 M KOH	11.09 F g ⁻¹	[32]
$CuCo_2O_4$	Bulk	2 A g ⁻¹ 3 M KOH	306 F g ⁻¹	[33]
CuCo ₂ O ₄	Nanoparticles	0.5 A g ⁻¹ 3 M LiOH	133 F g ⁻¹	[34]
MnCo ₂ O ₄	Flake	0.5 A g ⁻¹ 3 M LiOH	225 F g ⁻¹	[34]
MgCo ₂ O ₄	Nanoparticles	0.5 A g ⁻¹ 3 M LiOH	321 F g ⁻¹	[34]
NiCo ₂ O ₄	Nanoplates	1 A g ⁻¹ 1 M KOH	294 F g ⁻¹	[35]
CuCo ₂ O ₄ -C	Chrysanthemum-like	0.5 A g ⁻¹ 6 M KOH	335.8 F g ⁻¹	Our work

Table 1. The electrochemical capacitance values of different electrode materials

Table 1 summarizes previous results from similar supercapacitor electrode materials. It is worth noting that our results are superior to those of other systems. The impressive performance is likely due to the peculiar structure of $CuCo_2O_4$ -C. First, the highly porous chrysanthemum-like structure contains more open spaces, exposing more atoms and allowing for fast ion diffusion and charge transfer into the electrolyte and inner electrode. Second, the enhanced specific surface area provided a number of electrochemically active sites, which facilitated the redox reaction on the electrode surface and eventually improved the electrochemical performance. On the basis of the above description, we concluded that $CuCo_2O_4$ -C is a promising electrode material for supercapacitors.

4. CONCLUSIONS

In summary, we have illustrated a facile hydrothermal method to synthesize CuCo₂O₄ crystals

showed that the CuCo₂O₄-C electrode had a high specific capacitance of 335.8 F g⁻¹ (at a current density of 0.5 A g⁻¹), remarkable cycling stability (85% retention after 2000 cycles at a current density of 3 A g⁻¹) and excellent rate capability. To sum up, we synthesized chrysanthemum-like CuCo₂O₄-C crystals utilizing a facile method and low-cost precursors. These results demonstrated that the material has great potential for supercapacitor electrode applications.

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