



One-step synthesis of copper-cobalt carbonate hydroxide microsphere for electrochemical capacitors with superior stability



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ABSTRACT

Copper cobalt carbonate hydroxide (Cu-Co CH) microspheres were synthesized as a pseudocapacitive electrode material via a simple one-step hydrothermal method. Morphological characterization of the Cu-Co CH microspheres was carried out by scanning electron microscopy and transmission electron microscopy, showing their dandelion-like structure with the size approximately 4–7 μm . The crystalline structure, morphology and electrochemical performances of Cu-Co CH materials could be readily dominated by the molar ratio of Cu to Co. Among various stoichiometries of Cu-Co CHs, sample $\text{Cu}_{0.48}\text{Co}_{1.52}$ CH delivered the highest specific capacitance of 397.3 F g^{-1} at 1 A g^{-1} with a good rate capability. $\text{Cu}_{0.48}\text{Co}_{1.52}$ CH electrode material also exhibited a remarkably excellent cycling stability, $\sim 99\%$ of initial capacitance retention even after 10,000 charge/discharge cycles at 2 A g^{-1} . An asymmetric energy storage device was assembled by using $\text{Cu}_{0.48}\text{Co}_{1.52}$ CH as positive electrode and activated carbon as negative electrode in 2 M KOH electrolyte. The hybrid capacitor device could deliver an energy density of 26.3 Wh kg^{-1} at a power density of 400.2 W kg^{-1} , and remain 16.7 Wh kg^{-1} at 8374.2 W kg^{-1} . Meanwhile, it also showed amazing stability with $\sim 99\%$ capacity retention after 10,000 cycles. Based on the above results, Cu-Co CH microspheres possessed practical application as electrode materials for electrochemical capacitors due to their good structural stability in KOH electrolyte.

1. Introduction

Electrochemical capacitors (ECs) are new energy storage devices, which have attracted a lot of research interest due to their high power density, fast charge and discharge processes as well as promising potential applications [1–5]. It is well known that the performances of ECs are strongly dependent on the electrode materials [6,7]. Representative electrode materials for ECs are carbon materials [8,9], transition metal oxides/hydroxides [10], conductive polymers [11] and their composites [12,13].

Carbon due to its different allotropes, various structures and ability for existence under different dimensionality represents an attractive electrode material for ECs [8,14]. But, it is restricted by relatively low specific energy density which can be easily eliminated by the employment of transition metal oxides and hydroxides [7]. Cheng and co-workers fabricated $\text{NiCo}_2\text{O}_4@/\text{NiMoO}_4$ core-shell arrays on Ni foam by two-step method and the optimized electrode delivered a high areal capacitance of 5.8 F cm^{-2} at 10 mA cm^{-2} [15]. Xue et al. reported the dual-template synthesis of $\text{Co}(\text{OH})_2$ mesoporous nanowires which had a high specific capacitance of 993 F g^{-1} at 1 A g^{-1} [16]. Although there

are huge progresses that have been made on these transition metal based oxides and hydroxides, poor cycling stability of them still hinders their applications in high performance ECs.

In recent years, metal carbonate hydroxides (M-CHs) have attracted some research attention owing to their better cycling stability compared with metal oxides/hydroxides and higher specific capacitance than carbon materials. Some researchers have demonstrated that some metal carbonate hydroxide materials can effectively reduce the polarization of the electrode during the charge and discharge processes [17]. Masikhwa et al. synthesized a composite of cobalt hydroxide carbonate/activated carbon which showed a specific capacitance of 301.44 F g^{-1} at 1 A g^{-1} and exhibited an excellent cycling stability [18]. Furthermore, binary transition M-CHs can provide high electroconductivity and stable crystal structure due to their rich redox reactions and favorable synergistic effects, thus producing a high energy storage capacity [19,20]. Up to now, Ni-Cu and Ni-Co binary M-CHs have been explored as electrode materials for ECs. For instance, Zheng et al. fabricated ultrafine Ni-Cu CH nanowires on copper foam, and they exhibited a specific capacitance of 971 F g^{-1} at 1 A g^{-1} [21]. Li et al. synthesized Ni-Co CHs which achieved a high specific capacitance of

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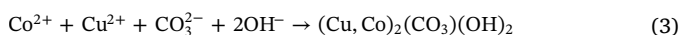
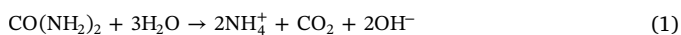
1019.2 F g⁻¹ at 1 A g⁻¹ [22]. However, Cu-Co CHs have not been widely investigated yet, despite their oxides/carbonates/hydroxides have been extensively studied in EC applications [23], which can be ascribed to the fact that it is not easy to obtain Cu-Co CHs with good crystallinity and high homogeneity. Liu et al. synthesized Cu-Co CHs which possessed a high specific capacitance of 789 F g⁻¹ at 1 A g⁻¹, but the synthesized Cu-Co CHs showed a moderate electrochemical stability, approximately 77.5% of specific capacitance retention after 3000 cycles at current density of 5 A g⁻¹ [23]. It was found that the molar ratio of Cu to Co was a key factor to control the morphology and structure of the product, which strongly affected the electrochemical performances of the electrode materials [24]. We found that it was easy to form a fixed proportion compound (Cu_{0.51}Co_{0.49}(CO₃)_{0.43}(OH)_{1.14}) when the reaction temperature was as low as 120 °C. The compound had a low conductivity and massive structure which were adverse to ion transfer between the electrode and electrolyte [25].

In this work, we fabricated a distinctive morphology of Cu-Co CHs which had a large surface area and high conductivity by a facile hydrothermal method at a moderate temperature. Cu-Co CHs materials with different Cu/Co ratios of 1:1, 1:2, 1:4, 1:6 and pure Co CH were synthesized. It was found that the Cu-Co CH products had the same dandelion-like structure in different compositions, which were totally different from the structure reported previously [26], however pure Co CH showed a nanoplate cluster. An increasing specific capacitance occurred with the increase of Co content and then attained a maximum value when the mole fraction of Co was 76% (Cu_{0.48}Co_{1.52} CH). The optimized electrode material showed a specific capacitance of 397.3 F g⁻¹ at 1 A g⁻¹. These results proved that the molar ratio of Cu to Co played a crucial role in their electrochemical properties. Significantly, ~99% of the capacitance could be retained after 10,000 charge/discharge cycles at 2 A g⁻¹, showing an extraordinary good cycling stability. An asymmetric supercapacitor was fabricated by using Cu_{0.48}Co_{1.52} CH electrode as positive electrode and activated carbon as negative electrode. It exhibited a high power density of 8374.2 W kg⁻¹ at an energy density of 16.7 Wh kg⁻¹, a high energy density of 26.3 Wh kg⁻¹ at a power density of 400.2 W kg⁻¹ and excellent cycling stability with ~99% capacity retention after 10,000 cycles at 5 A g⁻¹.

2. Experimental

2.1. Preparation of electrode materials and electrode

All the reagents used in the experiments were analytical grade and used without further purification. The Cu-Co CHs were synthesized by a hydrothermal method as follows. The total content of Cu(NO₃)₂ and Co(NO₃)₂ in the reaction solution was 3.5 mmol. Different Cu/Co molar ratios of 1:1, 1:2, 1:4, 1:6 and 0:1 were selected. A specific amount of Cu(NO₃)₂·3H₂O, Co(NO₃)₂·6H₂O and 14 mmol urea were dissolved in 35 mL deionized water. After being stirred for about 30 min, the transparent solution was transferred into a 100 mL Teflon-lined stainless autoclave and kept at 150 °C for 2 hours reaction to allow the growth of Cu-Co CH crystals. The thermolysis of urea is the rate-determined step of the total reaction. The mechanism of the synthesis process is as follows.



After reaction, the resultant solution was filtrated and fully washed by deionized water and ethanol, respectively, then dried at 80 °C for 10 h.

The electrodes were prepared according to the following steps. 80 wt% of Cu-Co CHs was mixed with 10 wt% of carbon black and 10 wt% of polyvinylidene fluoride, then they were dispersed in some 1-

methyl-2-pyrrolidone to form a homogeneous slurry. Afterwards, the slurry was coated onto a piece of Ni foam (NF, 1.5 cm × 1.5 cm) as a current collector. The electrodes were dried at 80 °C for 10 h before measurement. The mass loading of electrode material on each electrode was approximately 5 mg.

2.2. Materials characterization

The phase and crystal structure of Co-Cu CH were characterized by a powder X-ray diffractometer (PANalytical, Empyrean) using Cu-Kα irradiation (λ = 1.5406 Å) from 10° to 80°. A scanning electron microscope (SEM, Hitachi S-4800) and a transmission electron microscope (TEM, Philips-CM200) were used to characterize the morphology and microstructure. The element compositions of the samples were measured by an electron dispersive X-ray spectrometer (EDS) coupled with the SEM. Fourier transformed infrared spectrum (FTIR) was characterized by Bruker spectrometer (TENSOR27). The chemical analyses of the samples were also measured by X-ray photoelectron spectroscopy (XPS, Shimadzu, AXIS Supra).

2.3. Electrochemical measurements

The electrochemical measurements were carried out under a standard three-electrode system in 2 M KOH aqueous solution as electrolyte. The as-prepared electrode, nickel foil and Ag/AgCl electrode were used as working electrode, counter electrode, and reference electrode, respectively. Cyclic voltammograms (CV), galvanostatic charge/discharge curves and electrochemical impedance spectrum (EIS) were measured by a CHI660D electrochemical workstation. The cycle stability was tested in LAND CT2001A test system by galvanostatic charge/discharge processes. The EIS data were measured within the frequency range from 100 kHz to 0.01 Hz. The specific capacitances (C_s) of the samples were calculated according to the following equation.

$$C_s = I \cdot \Delta t / (m \cdot \Delta V) \quad (4)$$

where I (A), Δt (s), m (g) and ΔV (V) represent the discharge current, discharge time, mass of active material and potential window, respectively.

An asymmetric device, i.e. Cu-Co CH//activated carbon hybrid capacitor, was assembled by using optimized Cu-Co CH as positive electrode, activated carbon as negative electrode, 2 M KOH as electrolyte and a piece of cellulose paper as the separator. The mass ratio of Cu-Co CH to activated carbon was 1.35, which was calculated based on the charge balanced theory [27]. The performance of the hybrid capacitor was measured under two-electrode system.

3. Results and discussions

3.1. Composition and morphology analysis

The as-synthesized Cu-Co CH materials were first examined by EDS to determine their actual atomic percentages (at.%) of C, O, Cu and Co in each sample (in Fig. S1–S4). The exact Cu/Co molar ratios in the Cu-Co CH samples are listed in Table 1. The compositions of the samples which were prepared with Cu/Co molar ratio of 1:1, 1:2, 1:4, 1:6 were designated as Cu_{0.90}Co_{1.10} CH, Cu_{0.65}Co_{1.35} CH, Cu_{0.48}Co_{1.52} CH and

Table 1
The exact Cu/Co ratios of all samples.

Cu to Co ratio in solution	Measured Cu/Co ratio
1:1 Cu-Co CH	0.82
1:2 Cu-Co CH	0.48
1:4 Cu-Co CH	0.32
1:6 Cu-Co CH	0.21

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