

Facile synthesis of CuCo_2O_4 composite octahedrons for high performance supercapacitor application

Ashok Kumar Das^{a,c}, Nam Hoon Kim^b, Seung Hee Lee^a, Youngku Sohn^{c,*}, Joong Hee Lee^{a,b,*}

^a Advanced Materials Institute for BIN Convergence Technology (BK21 Plus Global Program), Department of BIN Convergence Technology, Chonbuk National University, Jeonbuk, Jeonju, 54896, Republic of Korea

^b Carbon Composite Research Center, Department of Polymer-Nano Science and Technology, Chonbuk National University, Jeonbuk, Jeonju, 54896, Republic of Korea

^c Department of Chemistry, Chungnam National University, Daejeon, 34134, Republic of Korea

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ABSTRACT

Shape tailoring of active materials could alter the performance of supercapacitors. Herein, we report the ethylenediaminetetraacetic acid (EDTA) assisted hydrothermal approach for the synthesis of single crystalline CuCo_2O_4 octahedrons and their application in a supercapacitor. Morphology and BET surface area analysis demonstrates the formation of CuCo_2O_4 octahedrons with a surface area of $61.97 \text{ m}^2 \text{ g}^{-1}$. As an active material, the CuCo_2O_4 octahedrons exhibited a high specific capacity of 989 C g^{-1} at 5 mV s^{-1} . In addition, a long-term cyclic stability with 87% of its initial specific capacity retention was achieved after 5000 cycles at 10 A g^{-1} . This outstanding performance could be ascribed to its unique octahedron morphology. The electrochemical results demonstrate that CuCo_2O_4 with such a unique octahedron architecture could be a potential active material for the development of a high performance supercapacitor.

1. Introduction

Increasing concerns about the global energy crisis have motivated significant research into the development of energy conversion and storage devices [1–6]. To address this issue, fuel cells, batteries, and supercapacitors have emerged as potential candidates to meet the future energy requirement [7]. Among these devices, the development of the supercapacitor has attracted worldwide attention as it has high power density, fast charge/discharge ability, longer cyclic stability, and wide operating temperature ranges [8]. Typically, transition metal oxide based supercapacitors deliver superior performance over the carbonaceous materials based supercapacitors [9], making them an ideal candidate for supercapacitor application. This active material dependent supercapacitive performance reveals that the exploration of several new transition metal oxide active materials and their application in the development of supercapacitors could lead to achievement of high specific capacitance, excellent cyclic stability, and high rate capability. Related to this, in the recent past, several transition metal oxides [10] and mixed transition metal oxide spinels [11] have been synthesized and used in the development of high performance supercapacitors. Among the various mixed transition metal oxide spinel

active materials, CuCo_2O_4 spinel has been recognized as a potential candidate not only in electrocatalysis [12] and Li-ion battery [13] applications but also in the area of supercapacitors [14] because of its low cost, abundance, and non-toxic nature as well as its two-fold higher electronic conductivity and supercapacitive performance compared to either single component copper oxide or cobalt oxide [15]. The capacitance in pseudocapacitive active materials such as CuCo_2O_4 originates from the interfacial redox reactions. Therefore, synthesis of pseudocapacitive active materials with an appropriate morphology is a vital issue, as their morphology could either enhance or diminish both electrode-electrolyte interface and the rate of ion transfer during the electrochemical reaction [16]. In earlier reports, it has been demonstrated that the performance of the supercapacitor varies considerably depending on the structure or surface morphology of the active materials [17]. In principle, by tuning the morphology of CuCo_2O_4 by adopting several synthetic approaches, the specific capacitance and power density of the supercapacitor could be closely regulated [18]. Until now, several attempts have been made for the synthesis of CuCo_2O_4 with different morphologies and their supercapacitive performance has been investigated [15,19–29]. For example, in the recent past, several CuCo_2O_4 micro/nanostructures such as nanograsses [15],

* Corresponding author. Advanced Materials Institute for BIN Convergence Technology (BK21 Plus Global Program), Department of BIN Convergence Technology, Chonbuk National University, Jeonbuk, Jeonju, 54896, Republic of Korea.

** Corresponding author.

E-mail addresses: youngkusohn@cnu.ac.kr (Y. Sohn), jhl@chonbuk.ac.kr (J.H. Lee).

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flower-like nanosheets [19], highly ordered mesoporous nanowires [20], hierarchical nanobelts [21], flowers [22], porous nanowires [23], nanowires [24], cauliflowers [25], nanosheets [26], maguery-like nanowires [27], cedar leaf-like [28], and hierarchical mesoporous 3D flower-like morphology [29] etc. have been synthesized and used in the fabrication of supercapacitors. Although several reports are available on the shape controlled synthesis of various CuCo_2O_4 micro/nanostructures, reports on the synthesis of CuCo_2O_4 polyhedrons are rare [13,30]. Most importantly, the synthesis of CuCo_2O_4 octahedrons and their application in supercapacitors has not yet been reported.

Hence, in this paper, we report a facile hydrothermal method for the EDTA assisted synthesis of CuCo_2O_4 octahedrons and their application as an active material for a supercapacitor. The unique octahedron morphology tailoring of CuCo_2O_4 resulted in a specific capacity of 989 C g^{-1} at a scan rate of 5 mV s^{-1} , together with an excellent cyclic stability capable of retaining 87% of its initial specific capacity after 5000 cycles at 10 A g^{-1} . Achievement of such a remarkable supercapacitive performance for the CuCo_2O_4 octahedrons suggests that it could be a potential active material for supercapacitor application.

2. Experimental

2.1. Materials

Ethylenediaminetetraacetic acid (EDTA), activated carbon, $\text{CuCl}_2 \cdot 6\text{H}_2\text{O}$, and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ were received from Sigma-Aldrich (Germany). Ammonium hydroxide (NH_4OH) solution, poly (vinylidene fluoride) (PVDF), N-methyl-2-pyrrolidone (NMP) and potassium hydroxide (KOH) were purchased from Samchun Pure Chemical Co. Ltd. (Korea). All solutions used in this investigation were prepared using Millipore water (Milli-Q system).

2.2. Synthesis of CuCo_2O_4 octahedron

CuCo_2O_4 octahedrons were synthesized using the hydrothermal method followed by calcination at 200°C , as schematically shown in Scheme 1. In a typical synthesis, 5 mM of $\text{CuCl}_2 \cdot 6\text{H}_2\text{O}$ and 10 mM of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ were mixed in 50 mL of deionized (DI) water under vigorous stirring for 5 min. Afterwards, 0.4 M EDTA was added to the above solution followed by the addition of a sufficient volume of NH_4OH to adjust the pH of the precursor solution to 14. The solution was then stirred for another 30 min. After 30 min stirring, all of the precursor solution was tightly sealed in a 100 mL Teflon autoclave for hydrothermal reaction for up to 12 h at 200°C . The autoclave was allowed to cool to room temperature naturally to achieve Cu-Co hydroxide precipitates. These precipitates were washed by centrifugation for several times using a water/ethanol mixture and dried at 60°C for 12 h. Finally, the Cu-Co hydroxide precipitates were calcined in air at 400°C

for 4 h at a heating rate of 2°C min^{-1} to achieve CuCo_2O_4 octahedrons. For comparison, another CuCo_2O_4 sample was prepared following the above method with the exclusion of the EDTA addition to the reaction mixture.

2.3. Characterization

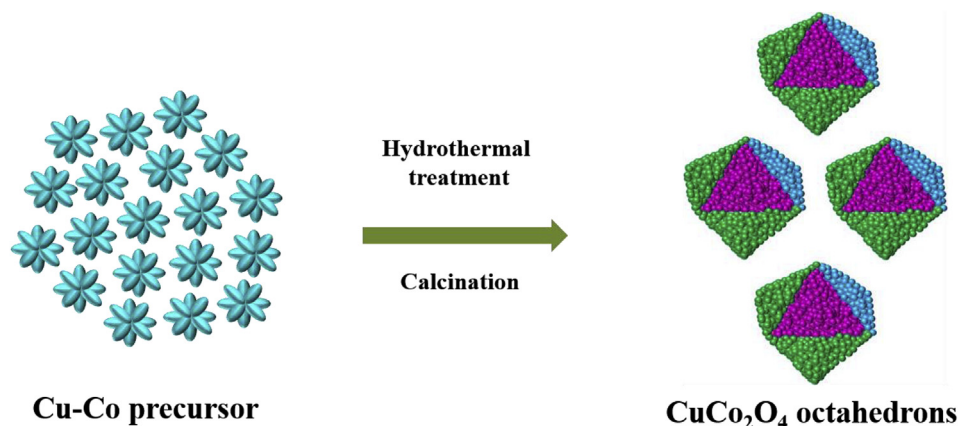
The CuCo_2O_4 samples were characterized by Fourier transform infrared spectroscopy (FTIR; Thermo Scientific Nicolet iS10 with a diamond crystal tip), X-ray diffractometry (XRD; PANalytical X'Pert Pro MPD, Cu-K α target, $\lambda = 1.5406 \text{ \AA}$), Raman spectroscopy (Nanofinder 30 system, Tokyo Instruments Co., Osaka, Japan), field emission scanning electron microscopy (FESEM; SUPRA40VP, Carl Zeiss, Germany), transmission electron microscopy (TEM; JEOL JEM-2200 FS, Japan), and Brunauer-Emmett-Teller surface area (BET; Micromeritics Tristar 3000) measurement techniques. For TEM and high resolution TEM (HRTEM) image recording the samples were casted on the carbon coated Ni grid. The supercapacitive performance investigation (Zive-SP1 electrochemical workstation, Wonatech, Korea) was carried out in 6 M KOH electrolyte in a three-electrode mode. The carbon paper was coated with CuCo_2O_4 sample slurries, Pt wire, and Ag/AgCl (3 M NaCl) acted as the working, counter, and reference electrodes, respectively. For working electrode preparation, the slurries of the active electrode materials were first prepared in 2 mL NMP solvent by mixing 6 mg of either CuCo_2O_4 octahedron or quasi-spherical CuCo_2O_4 nanoparticles, 2 mg PVDF and 2 mg activated carbon. These slurries were completely transferred onto the carbon paper substrate within a $1 \text{ cm} \times 1 \text{ cm}$ area by drop casting method followed by overnight drying at 60°C .

3. Results and discussion

3.1. Characterization of quasi-spherical and octahedron shaped CuCo_2O_4 nanoparticles

3.1.1. XRD analysis

The crystal planes present in the CuCo_2O_4 samples were investigated by XRD analysis and their diffraction patterns are presented in Fig. 1. In the case of the quasi-spherical CuCo_2O_4 nanoparticles, nine peaks were observed and were ascribed to the (111), (220), (311), (222), (400), (422), (511), (440), and (533) planes of the CuCo_2O_4 spinel. While the CuCo_2O_4 octahedrons possess similar peaks, these peak intensities are higher than those of the planes present in the quasi-spherical CuCo_2O_4 nanoparticles. The (311) plane of the CuCo_2O_4 octahedron and quasi-spherical CuCo_2O_4 nanoparticle is significantly more intense than the other planes and is the highest plane in the CuCo_2O_4 octahedron case. In both CuCo_2O_4 samples, except for the peaks corresponding to the CuCo_2O_4 spinel, no other additional peaks were noticed, supporting the formation of highly crystalline and



Scheme 1. Schematic representation of the synthesis of CuCo_2O_4 octahedrons.

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