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# Binary composite of polyaniline/copper cobaltite for high performance asymmetric supercapacitor application

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ABSTRACT

This article presents the effect of polyaniline (PANI) embedded copper cobaltite ($CuCo_2O_4$) as an electrode material for high performance supercapacitor application. The composite of PANI-$CuCo_2O_4$ was prepared via blending process. The formation of PANI-$CuCo_2O_4$ composite was confirmed by X-ray diffraction (XRD) and Fourier transform infrared (FTIR) analysis. The surface morphologies showed that the spinel structure of $CuCo_2O_4$ (average particle size of 30 nm) was well distributed on PANI matrix, suggest the effective intercalation of $CuCo_2O_4$ with PANI matrix. The electrochemical properties of $CuCo_2O_4$, PANI and PANI-$CuCo_2O_4$ composite were investigated using cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) in 1 M of KOH as an aqueous electrolyte. The PANI-$CuCo_2O_4$ composite showed the improved specific capacitance of 403C/g than that of pure $CuCo_2O_4$ and PANI.The enhanced electrochemical performance was obtained due to the augmentation of redox active sites and synergetic effect between PANI and $CuCo_2O_4$ nanoparticles. Additionally, the fabricated (activated carbon (AC)/PANI-$CuCo_2O_4$) asymmetric supercapacitor device can be cycled reversibly at a cell voltage of 1.5 V, which exhibited excellent electrochemical performances with an energy density of 76 Wh/kg and a power density of 599 W/kg. It also presented a superior life cycle with 94% capacitance retention after 3000 cycles.



## 1. Introduction

Supercapacitors are receiving extensive attention due to their efficient capability of storing and discharging energy than that of other primary energy sources like fuel cells and batteries. In recent years, several works have been developed in order to get the high energy density, long cycling life and low internal resistance based energy system [1,2]. However, still, we have some limitation to develop the practical applications due to the lack of appropriate electrode materials with optimal electrochemical properties. Generally, there are two different ways to store the energies such as capacitive (electric double layer capacitors (EDLCs)) and pseudocapacitive (pseudocapacitor) nature. In EDLCs, the capacitance arises from the adsorption of electrolyte ions on the electrode/electrolyte interface without involve faradaic reaction leading to high power density. While for pseudocapacitors, the capacitance arises from the reversible faradaic reactions at the surface of electrode material as well as the insertion of cations from the electrolyte [3–5]. Ruthenium oxide ($RuO_2$) has been recognized as the best pseudocapacitive material due to its high specific capacitance, good electrical conductivity and reversible charge-discharge properties [6,7]. However, there are some limitations to use $RuO_2$ as an electrode material in a commercial scale such as expensive and high toxicity.

In recent years, it has been demonstrated that spinel structure of transition metal oxides is an effective strategy to improve the performance of single-component metal oxides such as nickel cobaltite ($NiCo_2O_4$), zinc cobaltite ($ZnCo_2O_4$), cobalt ferrite ($CoFe_2O_4$), manganese cobaltite ($MnCo_2O_4$) and etc [8–11]. The presence of two metal oxides within the one molecule exhibited better physico-chemical properties such as good electrical conductivity, high stability and improved redox sites with numerous oxidation states than that of single metal oxides [12]. Among these spinel metal oxides, $CuCo_2O_4$ has been realized as a good electrode material for supercapacitor application. $CuCo_2O_4$ spinel has unique structure where divalent Cu ions occupy the

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tetrahedral site and the trivalent Co ions occupy the octahedral site in the cubic spinel structure. In addition, $CuCo_2O_4$ offers several advantages including abundant resources, low cost and environmental friendliness [13]. However, the capacitance and operation voltage are still the challenging task to improve the supercapacitor performance.

Polyaniline (PANI) is one of the most interesting and widely used conductive polymers in various applications such as batteries [14], sensors [15] and supercapacitor [16]. PANI has several advantages in terms of good electrical conductivity, high electrochemical activity, chemical stability, excellent redox properties, low cost and flexibility. In general, PANI exhibiting three different structural forms such as fully reduced state (leucoemeraldine), fully oxidized state (pernigraniline) and half-oxidized state (emeraldine base) [17]. Herein, the emeraldine form is the most conductive part and also is the key factor to enhance the electrochemical activity.

The present work is investigating the electrochemical performance of $CuCo_2O_4$ intercalated PANI matrix. The improved electrochemical properties in spinel structured $CuCo_2O_4$ are offered by the incorporation of PANI, which lead to restrict the aggregation of $CuCo_2O_4$ with improved electrochemical surface area. To the best of our knowledge, no attention has been paid to the comparison between the pure $CuCo_2O_4$ and the PANI-$CuCo_2O_4$ composite especially for supercapacitor application. In addition, the performance of PANI-$CuCo_2O_4$ in asymmetric supercapacitor is also studied.

## 2. Materials and method

### 2.1. Materials

Copper acetate dihydrate, $Cu(O_2CCH_3)_2{\cdot}2H_2O$ and cobalt acetate tetrahydrate $Co(C_2H_3O_2)_2{\cdot}4H_2O$ were purchased from Friendemann Schmidt, Malaysia. Urea, ammonia (28% purity), aniline, ammonium peroxydisulfate (APS), hydrochloric acid (HCl), polyvinylidene fluoride (PVdF), acetylene black and activated carbon (AC) were received from Sigma-Aldrich, Malaysia. Ethanol (95% purity) was purchased from J. Kollin Chemical, Malaysia.

### 2.2. Synthesis of polyaniline (PANI)

PANI was synthesized by chemical oxidation polymerization method. 0.25 M aniline was added into 20 ml of 1 M aqueous HCl. The solution was stirred at room temperature for the formation of anilinium ions. Next, the freshly prepared APS solution (0.2 M APS dissolved into 30 ml of 1 M HCl) was added dropwise into the above solution and allowed for continuous stirring until a green precipitate observed. Then the precipitate was washed with acetone and deionized water for several times and dried at 60 °C for 1 h. Finally, the observed green color was the evidence of the polyaniline formation in its conductive form of emeraldine salt (ES).

### 2.3. Synthesis of $CuCo_2O_4$ nanoparticles

$CuCo_2O_4$ nanoparticles were synthesized by a simple hydrothermal treatment. $Cu(O_2CCH_3)_2{\cdot}2H_2O$ (15 mmol), $Co(C_2H_3O_2)_2{\cdot}4H_2O$ (15 mmol), urea (20 mmol) and 3.4 mL of ammonia were added into the solution of water-ethanol mixture and stirred for 19 h. Next, the mixture was transferred into a 80 mL capacity of Teflon-lined stainless steel autoclave, which was heated and maintained at 180 °C for 6 h. After that the obtained sample was washed with deionized water for several times to remove the redundant materials and then dried at 60 °C.

### 2.4. Synthesis of PANI-$CuCo_2O_4$ nanoparticles

PANI-$CuCo_2O_4$ nanocomposite was prepared by blending of PANI with $CuCo_2O_4$ (weight ratio of PANI:$CuCo_2O_4$ = 4:1) in a pestle mortar to achieve a homogeneous mixture of PANI with $CuCo_2O_4$ composite. The entire preparation process was schematically illustrated in Fig. 1.

### 2.5. Characterization of the samples

The crystalline phases of the samples were determined via X-ray diffraction (XRD; D5000, Siemens), using copper $K_\alpha$ radiation ($\lambda$ = 1.5418 Å) at a scan rate of 0.02° $s^{-1}$. The morphological studies of synthesized pure $CuCo_2O_4$ nanoparticles, pure PANI and PANI-$CuCo_2O_4$ composite were carried out using JEOL JSM-7600F, field emission scanning electron microscopy (FESEM). Fourier transform infrared spectroscopy (FTIR, Thermo Scientific Nicolet ISIO Smart ITR) analysis used to study the presence of functional groups and purity of samples, which was in the region from 400 to 2500 $cm^{-1}$ at a resolution of 1 $cm^{-1}$.

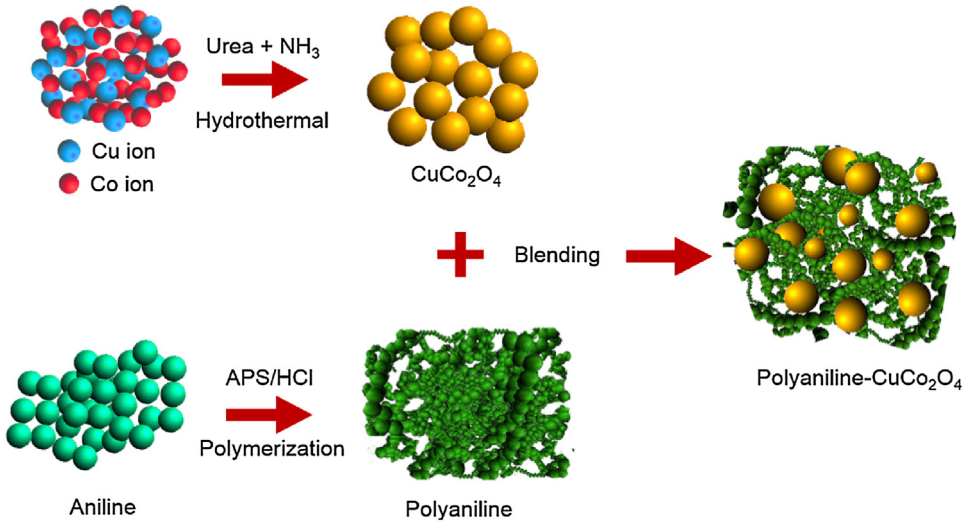


**Fig. 1.** Schematic diagram of PANI-$CuCo_2O_4$ composite preparation.