Conjugated Cobalt (II) Polyphthalocyanine Doped with Carbon Nanotubes as Available Electrode for Supercapacitors

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Abstract. The use of organic compounds to meet the growing demand for new energy storage systems has attracted great attention, because they have the advantages of abundant resources, flexibility, and sustainability, which can be used as supercapacitor electrode materials. In this work, based on the synthetic metal polyphthalocyanine, carbon nanotube-doped conjugated cobalt (II) -polyphthalocyanine film was further used as an electrode material for supercapacitors. The results show that the obtained CoPPc-CNT has good electrochemical performance. The results show that by combining an organic material with a carbon matrix to prepare a composite material, the electronic conductivity can be effectively improved for supercapacitors.

1. Introduction
With the rapid growth of fossil fuel consumption, the resulting environmental pollution problem has caused a huge demand for energy [1]. In our daily life, electrochemical energy storage (EES) devices are becoming increasingly crucial [2]. Among the kinds of energy storage devices, supercapacitors (SCs) are extremely desirable and attractive [3]. Because they have the advantages of high power density, low cost, wide operating temperature range, good cycle stability and excellent reversibility [4-6]. According to the mechanism of charge, SCs can be sorted into three types, which are pseudocapacitors, electric double layer capacitors (EDLCs) or faradaic capacitors [7].

In recent decades, organic conjugated polymers, carbon materials and transition metal compounds [8-10] have exhibited good performances as electrode materials for SCs. Phthalocyanine complexes are motivating for research because they also possess nitrogen active sites along with metal centers capable of redox reactions [11]. There is huge interest to actively explore transition metal complexes as potential electrode systems for supercapacitor applications [12]. Apart from this, several types of EDLC materials have been utilized as SCs electrodes. These includes graphene, carbide-derived carbons, carbon-nanofibers, carbon nanotubes (CNTs) and activated carbon [13-14]. The method of direct synthesis of compound transition metal organics composited with carbon materials, which can effectively improve electron conductivity.

In this report, we synthesized conjugated cobalt (II)-polyphthalocyanine doped with carbon nanotubes via solvothermal processes in one step for SCs. The reaction process is simple for one-step synthesis, save raw materials and avoid polluting the environment.
2. Experimental section

2.1. Materials
Ethanol (AR), 1,2,4,5-Tetracyanobenzene (AR), cobalt (II) chloride (CoCl₂, AR) and 1,8-Diazabicyclo [5.4.0] undec-7-ene (DBU, AR) were purchased from Aladdin Chemical Reagent Co., Ltd. The multiwalled carbon nanotube (CNTs, 90% purity; the diameter of ~10 nm and length of ~20 μm) were supplied by Cnano Technology Ltd. Unless otherwise specified, all materials were commercial reagents and can be used without further purification. The water used in our present work was deionized.

2.2. Instruments
Scanning electron microscopy (SEM) was performed by JEM-6701F (JEOL Ltd.). Fourier transform infrared spectra (FTIR) spectra were determined by PerkinElmer Frontier equipment using the KBr pellet technique. All the electrochemical measurements were performed on CHI660E Electrochemical Workstation (Shanghai Chenhua Instruments Co., Ltd.).

2.3. Preparation of conjugated cobalt (II)-polyphthalocyanine doped with carbon nanotubes (CoPPc-CNT)
The CoPPc-CNT was synthesized by the following procedure. First, CNTs (25 mg) were dissolved into ethanol (15 mL) and stirred with ultrasound for 30 min to form a suspension. Then, 1,2,4,5-Tetracyanobenzene (25 mg), CoCl₂ (9 mg) and DBU (21.5 mg) were mixed into the suspension and sonicated for 30 min continuously stirred for 24 h. And then, the suspension was put into a 25 mL of Teflon-lined stainless-steel container and dissolved in ethanol (5 mL) and reacted at 180 °C for 8 h. After cooling to room temperature, the product was collected by centrifugation and washed with ethanol and deionized water several times. Finally, the solid was freeze drying in freeze dryer oven overnight to get the product and the CoPPc-CNT film (as for the working electrode) was obtained by vacuum filtration.

2.4. Electrochemical measurement
All the electrochemical performances were regulated with a three-electrode system at the room temperature. The reference electrode was an Ag/AgCl electrode with saturated KCl solution, the counter electrode was a platinum foil and the working electrode was the CoPPc-CNT. The electrochemical measurements were finished using 1 M H₂SO₄ solution as electrolytes with potentials ranging from 0-0.9 V for SCs. The specific capacitance (C, F g⁻¹) for SCs was calculated by the following formula [15]:

\[ C = \frac{(I \times t)}{(m \times V)} \]  

(1)

In the formula, t is the time (s), I is the current (A), m is the load mass (g) of the active material and V is the voltage range.

3. Results and discussion
Figure 1 shows the synthesis process of CoPPc-CNT film, which is obtained by vacuum filtration. One-step synthesis of compound the CoPPc-CNT film by hydrothermal method of 1,2,4,5-Tetracyanobenzene, CoCl₂, DBU and CNTs, which has the advantages of cost saving and simple reaction.
Figure 1. The synthesis process of CoPPc-CNT.

FT-IR spectra provide information in the case of whether polymers containing structural elements. Compared to pure CNT, the FT-IR spectrum of CoPPc-CNT reveals additional bands. The FT-IR spectrum of CNT shows C=C vibration at 1570 cm\(^{-1}\), while the FT-IR spectrum of CoPPc-CNT shows C=O and C-C vibration at 1650 cm\(^{-1}\) and 1600 cm\(^{-1}\), respectively (Figure 2) [16].

Figure 2. FT-IR spectra of CoPPc-CNT compared with CNT.

Scanning electron microscopy (SEM) images confirm that the morphological characteristic of CoPPc-CNT showing the aggregation network morphology (Figure 3), which is similar to the common morphology of pure CNT.
Figure 3. SEM images of CoPPc-CNT.

The cyclic voltammetry (CV) and the galvanostatic charge/discharge (GCD) measurements were implemented to determine the electrochemical properties of CoPPc-CNT film as the working electrode. Figure 4a shows the cyclic voltammograms obtained at sweep rates 50 mV s⁻¹ within a potential window of 0 to 0.9 V in 1 M H₂SO₄ for CNT and CoPPc-CNT. The CV curve of CNT shows the typical electric double layer capacitor performance. In contrast, the integral area of the CV curve of CoPPc-CNT is significantly larger than that of pure CNT. That means the capacitance performance of CoPPc-CNT is stronger than pure CNT. Moreover, the GCD measurements of CNT and CoPPc-CNT at the current density of 1.0 A g⁻¹ is shown in Figure 4b. As shown in the figure, the GCD curve of CNT shows a symmetrical triangular shape. In addition, CoPPc-CNT not only exhibits a symmetrical triangular shape, but also the charge and discharge time is longer than pure CNT, showing better electrochemical performance. The specific capacitance of the CoPPc-CNT electrode calculated from the GCD curve and the corresponding formula is approximately 67.7 F g⁻¹ at the current density of 1 A g⁻¹. Compared with pure CNT, CoPPc-CNT shows the better electrochemical performance.

Figure 4. (a) CV curves of the samples at a scan rate of 50 mV s⁻¹. (b) GCD curves of the samples at 1.0 A g⁻¹.
4. Conclusions
In summary, conjugated cobalt (II) -polyphthalocyanine doped with carbon nanotubes was prepared by one-step reaction under solvothermal conditions, which could be used as electrode material for supercapacitors. CoPpC-CNT electrode exhibits good electrochemical performance, which may be attribute to the way of direct synthesis of transition metal organics doped with carbon materials. And the method can effectively improve the electronic conductivity. At the same time, the entire process has the advantage of saving costs and avoiding environmental pollution.

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