

Preparation of cobalt hydroxide nanosheets on carbon nanotubes/carbon paper conductive substrate for supercapacitor application



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ABSTRACT

Multi-walled carbon nanotubes grown on the carbon paper substrate are prepared by in situ growth in a chemical vapor deposition system. $\text{Co}(\text{OH})_2$ is deposited on carbon nanotubes/carbon paper by electrodeposition methods. SEM images show that the successful growth of nanometer-sized $\text{Co}(\text{OH})_2$ nanosheets on the surface of carbon nanotubes/carbon paper substrate. The electrodes of $\text{Co}(\text{OH})_2$ /carbon nanotubes/carbon paper composite are investigated for their use in supercapacitors with cyclic voltammograms, chronopotentiometric measurements and electrochemical impedance spectroscopy. The composite electrode shows the largest specific capacitance of 1083 F g^{-1} at a current density of 0.83 A g^{-1} in 6 M KOH electrolyte. Furthermore, this composite exhibits good cycling stability and lifetime. The implanted CNTs between carbon paper and $\text{Co}(\text{OH})_2$ act as a good conductive medium for electrodes in supercapacitors, and the interconnected nanosheets of the $\text{Co}(\text{OH})_2$ can facilitate the contact of the electrolyte with active materials, and thus increase the capacitance.

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1. Introduction

Supercapacitors are important sources for energy storage device in various applications such as military devices, consumer electronics, and portable electronic products due to their high power density, excellent reversibility and long cycle life [1–3]. Pseudocapacitive transition metal oxides and hydroxides have been widely studied as cathode materials for supercapacitors due to their much higher capacitances (several times) than double-layered carbonaceous materials [4,5]. $\text{Co}(\text{OH})_2$, because of its favorable capacitive characteristics and environmental friendliness, is generally considered as promising electrode materials for supercapacitors [6–11].

The performance of pseudocapacitive materials for supercapacitors is mainly determined by their electrochemical activity and kinetic feature of the electrodes. Thus, it is crucial to enhance the performance of charge storage/delivery inside the electrodes and electron transport at the electrode/electrolyte interface [12,13]. One way is to build the electroactive materials with nanostructure, which possesses short ion diffusion path and enlarged surface area. It provides more efficient contact between electrolyte ion and active materials for Faradaic energy storage. Recently, the synthesis of cobalt oxide/hydroxide with nanostructure, such as nanotubes [14], nanoflakes [15,16], nanorod [17] and nanoflowers

[18] has been reported. The other way is to construct the electroactive materials-conductive matrix hybrid nanostructures, in which the matrix acts as a highly porous conductive network enabling a good access of ions and electrons to the active surfaces leading to enhanced supercapacitor performances [19]. At present numerous efforts have been made to use Ni foam as substrates for loading the electroactive materials to obtain nanostructured electrodes [20,21]. The specific capacitance of these materials are high, even reach up to 3152 F g^{-1} [22]. Nevertheless, Xing et al. [23] found that the clean nickel foam itself did have capacitive properties in KOH electrolyte within positive potential window, which could bring the complexity of the measurement for specific capacitance values. Carbon paper (CP) would be ideal porous conductive substrate and current collector. Compared to Ni foam, CP is a synthetic thin, lightweight matrix with pore spaces on the micrometer scale, which is a significant advantage for supercapacitor applications. Recently, several groups have grown carbon nanotubes (CNTs) onto carbon substrate (e.g., carbon fabric or carbon paper), forming a carbon composite [24–28]. The CNTs grown carbon substrates offer an external surface area for supporting electroactive materials, compared to a pristine CP.

In our present work, a CVD approach was used to fabricate CNTs directly grown on as a three-dimensional matrix. Subsequently, nanometer-sized $\text{Co}(\text{OH})_2$ sheets were attached to the CNTs/CP substrates by using electrodeposition technique. It could be demonstrated that the electrochemical performances, such as specific capacitance and high rate capability of $\text{Co}(\text{OH})_2$ /CNTs/CP

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electrode can be greatly enhanced by using CNTs/CP as the substrate with three-dimensionally interconnected nanoporous structure. Between CP and Co(OH)_2 , the presence of CNTs can enhance the electrochemical activity and reduce charge transfer resistances, which is analyzed by electrochemical impedance spectroscopy.

2. Experimental

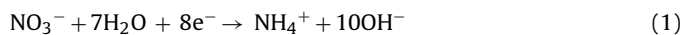
2.1. Synthesis of CNTs film

5 nm-thickness Fe thin films used for the catalyst in growing CNTs were deposited on the surface of the CP (Toray Inc.) using a radio frequency magnetron sputtering system. The input power for the sputter cathode was 50 W and the Ar gas pressure was 10 mTorr during the sputtering process. Porous, low-density CP, which was composed of graphite fibers with 7 μm diameter, was used as the current collector substrate. CNTs were grown using chemical vapor deposition (CVD) system. CVD was carried out at 700 °C by introducing a gas mixture of methane (CH_4 , 99.9%), hydrogen (H_2 , 99.99%) and argon. The flow rates of $\text{CH}_4/\text{H}_2/\text{Ar}$ were 80/40/200 sccm, respectively. The total gas pressure was 1 atm. The growth time was 30 min. The samples were furnace cooled under flowing Ar gas after the completion of deposition. A dark black layer of CNTs was formed on the top side of the carbon paper where surface modification was carried out. Since CNTs are hydrophobic in nature, the in situ grown CNTs/CP was treated with concentrated nitric acid at 140 °C for 15 h according to the procedure described in the literature [29]. Then the treated CNTs/CP was rinsed with distilled water and heated in muffle furnace at 300 °C for 30 min to improve the wetting characteristics. The acid treatment is a well-accepted process for functionalizing CNTs for incorporating carboxyl and hydroxide groups.

2.2. Electrochemical deposition of Co(OH)_2

All the chemical reagents used in this experiment were analytical grade and used as received without further purification. The surface area of CNTs/CP substrate for deposition was 1 cm^2 (1 $\text{cm} \times 1 \text{ cm}$). The CNTs/CP substrate was washed in acetone with ultrasonic for 30 min first, then washed with double-distilled water for several times, and dried in an oven at 100 °C.

The electrodeposition was performed in a standard three electrode glass cell. A 1 cm^2 platinum plate was used as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. Cobalt hydroxide films were directly deposited from 0.1 M $\text{Co(NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution at room temperature using a CHI760D electrochemical workstation (China). The deposition potential was -1.0 V vs. SCE. The electrodeposition process of the Co(OH)_2 film can be expressed as follows: [20]



After deposition process, Co(OH)_2 film on the CNTs/CP substrate was washed in distilled water and dried in an oven at 333 K for 12 h. The weight of the Co(OH)_2 film in the electrode was directly measured using the electronic microbalance (Sartorius, CPA225D, $d = 0.01/0.1 \text{ mg}$). The mass load of active material was measured in all the cases by subtracting the mass of substrate from the total weight.

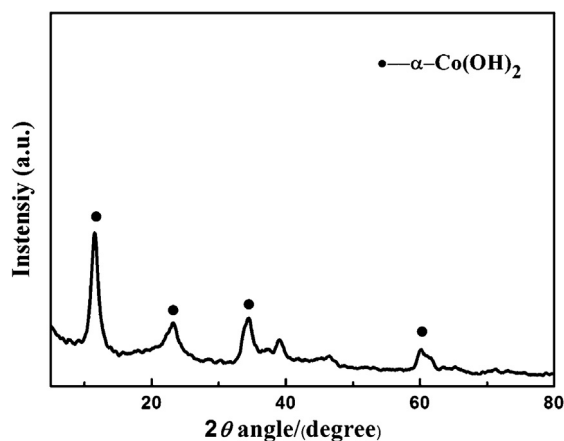


Fig. 1. X-ray diffraction patterns of electrodeposited $\alpha\text{-Co(OH)}_2$.

2.3. Material characterisations and electrochemical measurements

Transmission electron microscope (TEM) was carried out by using a JEOL JEM-2100 (Japan) operated at 200 kV. Morphology of the synthesized products was examined by using a SUPRA55 (German) field emission scanning electron microscope (SEM). Wide angle powder X-ray diffraction (XRD) patterns were obtained with a Rigaku D/Max-2400 (Japan) with Cu K α radiation (40 kV, 100 mA). Nitrogen adsorption–desorption data was obtained by using ASAP 2020 (Micromeritics, USA).

The electrochemical measurements were carried out in a half-cell setup configuration connected to an electrochemical workstation. A thin film on the CNTs/CP substrate (1 cm^2) was used as the working electrode. A platinum plate electrode and a SCE served as the counter electrode and the reference electrode respectively. Freshly prepared 6 M KOH aqueous solution was used as the electrolyte.

3. Results and discussion

The XRD patterns of the Co(OH)_2 nanostructure is presented in Fig. 1. The pattern consists of four peaks appearing at 2θ values of 11.4°, 22.6°, 33.7° and 61.1° with low crystallinity, and all the characteristic peaks belong to hydroxalite-like $\alpha\text{-Co(OH)}_2$ phase [30]. No obvious peaks of $\beta\text{-Co(OH)}_2$ have been observed in the XRD pattern of the composite, and it corresponds to the layered $\alpha\text{-Co(OH)}_2$ structure. Furthermore, the α -phase hydroxides display more disorder and a larger interlayer spacing as the interlamellar space which contains water molecules or other anions [31].

As can be seen in Fig. 2a, the CP is a highly porous three-dimensional network of carbon fibers, each of which has a diameter of ca. 7 μm , and the surface of these fibers are very clean before CNTs deposition. Fig. 2b shows the SEM image of the CNTs grown directly on the carbon fibers. All the carbon fibers are uniformly covered by a forest of CNTs of about 10 μm length in Fig. 2c. The high resolution TEM image in Fig. 2d shows that the CNTs are highly crystalline and the outer diameter and inner diameter are estimated as 5 and 12 nm, respectively. Fig. 2d also shows the nature of CNTs along with the fringes depicting the multiple number of layers in CNTs. As a result, a dense CNTs layer with porous nanostructure is obtained on the CP, and the surface of CP is modified by the dense CNTs layer where its high surface area and porosity are observed by means of SEM.

The SEM images of Co(OH)_2 films deposited at -1.0 V with different deposition times of 180 and 300 s are displayed in Fig. 3a–d. Fig. 3a and b show that Co(OH)_2 is heterogeneously nucleated

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