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Synthesis and characterization of $Co(OH)_2$/TiO_2 nanotube composites as supercapacitor materials

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Abstract A novel composite of $Co(OH)_2$ and TiO_2 nanotubes was synthesized by a chemical precipitation method. $Co(OH)_2$/TiO_2 nanotube composites and its microstructure were characterized by transmission electron microscopy (TEM), X-ray diffraction pattern (XRD). The electrochemical capacitance performance of this composite was investigated by cyclic voltammetry and charge–discharge tests with a three-electrode system in 6 M KOH solution. We synthesized different weight ratios of $Co(OH)_2$/TiO_2 nanotubes, a maximum specific capacitance of 229 F/g was obtained for the composite. Based on these tests, we propose that TiO_2 nanotubes provide the three-dimensional nanotube network structure for the composite and make the $Co(OH)_2$ dispersed. For these reasons, the TiO_2 nanotubes used as a framework for $Co(OH)_2$ improve the utilization of $Co(OH)_2$ greatly.

Keywords Composite · Utilization · Supercapacitors

Introduction

Recently, electrochemical supercapacitors attract more attentions in the energy storage, and conversion systems, which have higher energy density than dielectric capacitors and have higher power density than batteries [1], is being considered for a variety of applications such as in hybrid electric vehicles, uninterruptible power supplies, memory protection of computer electronics, and cellular devices [2, 3]. The materials studied for a capacitor have been mainly of three types: carbon/carbon [4], metal oxide [5–7], and electronically conducting polymer [8]. Though noble-metal oxides or hydrous oxides (i.e., ruthenium oxides) yield a remarkably large value of capacitance, the high cost of these materials limits its application [9–12]. Because of having very large theoretical capacitance, the cheap metal oxides or hydrous oxides are promising candidates for the materials of electrochemical supercapacitors. The cobalt compound capacitors, including CoO_x, Co_3O_4, and $Co(OH)_2$ are studied for the same reason [13–15], but the cobalt compounds, based on conventional methods, does not have satisfactory capacitance characteristics; so, enhancing the utilization of this material to improve its specific capacitance has been the focus of the present study for electrochemical supercapacitors. It is known that the specific surface area of electrodes is directly related to the specific capacitance because the high surface area produces the large reaction place and a lot of pores cause rapid transfer of the electrolyte. However, the specific surface area of the $Co(OH)_2$ is, in general, not high enough for high capacitance.

Titanium dioxide, as a popular nanomaterial, has numerous potential applications such as in photocatalysis [16], liquid solar cell [17], and electroluminescent hybrid device [18]. Its tubular structures, TiO_2 nanotubes, have been considered more practical in rechargeable lithium batteries and electrochemical supercapacitors [19]. Adding TiO_2 nanotubes in $Co(OH)_2$ electrode is, therefore, expected to provide a chance to improve the performance of the compounds. Although TiO_2 nanotubes is not suitable for electrochemical capacitors, it can make the metal oxides or

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hydrous oxides disperse and increase these utilization. Wang YG et al. [20, 21] have used TiO_2 nanotubes as a solid support to disperse metal oxides. However, another material, including $Co(OH)_2$, needs to be identified which exhibits capacitance by this simple method. In addition, it is desirable to study the generality of this method as a means of fabricating other hydrous oxide/TiO_2 nanotube composites for use in capacitor applications. In this paper, we synthesized a novel composite of $Co(OH)_2$/TiO_2 nanotubes by a chemical precipitation method. The goal of this work is to use this novel composite as the electrode material for electrochemical supercapacitors.

Experimental

Synthesis and characterization of TiO_2 nanotubes

TiO_2 nanotubes were synthesized via a hydrothermal chemical process [22]. Typically, 500 mg pure TiO_2 powders of anatase phase were mixed with 10 M NaOH aqueous solution in a Teflon vessel at 110 °C for 20 h. The resulted product was treated with 0.1 M HCl and further washed with distilled water.

Synthesis of $Co(OH)_2$/TiO_2 nanotube composites

Firstly, 0.5 g TiO_2 nanotubes were mixed with an aqueous solution (50 ml) containing proportional weight of Co($CH_3COO)_2 \cdot 4H_2O$ under stirring for 10 min. Then, aqueous solution of 0.1 M KOH was dropped into the mixed aqueous solution with vigorous stirring until the brown precipitation was formed. The final pH was adjusted to be around 9. Then, the producing precipitate was filtered, washed with distilled water several times and dried for 10 h under vacuum at 80 °C.

Synthesis of the composite electrodes

The working electrodes (20 mg) were prepared by mixing 80 wt% of $Co(OH)_2$/TiO_2 composite powder with 17.5 wt% of acetylene black (>99.9%) and 2.5 wt% of poly(tetra-flouoroethylene) dried powder (PTFE). The first three components were mixed together in an agate mortar until homogeneous black powder was achieved. PTFE was then added to the mixture with a few drops of ethanol. The synthesized paste was pressed at 20 Mpa to a nickel gauze and dried for 10 h under vacuum at 80 °C.

Characterization of the composites

Electrochemical studies were carried out using an electrochemical working station (CHI-660, Chenhua, Shanghai).

All the electrochemical measurements were done in a three-electrode arrangement. A platinum gauze and a saturated calomel electrode (SCE) were used as a counter electrode and reference electrode, respectively. All measurements were carried out in 6 M KOH electrolyte. Electrochemical performance was characterized by cyclic voltammetry with a voltage scan rate 10 mV/s. The impedance properties of the electrodes were examined by impedance spectroscopy at an applied potential of 0 V by using a CHI660 electrochemical work station. Data were collected in the frequency range of 10^5 to 10^{-2} Hz at an applied potential of 0 V. The galvanostatic charge/discharge of the electrode was evaluated in the certain range of potential at the current of 2, 5, and 10 mA.

The structural morphology of synthesized nanoparticle alloys were observed on a FEI-Tecnai G^2 20 S-TWIN transmission electron microscopy (TEM). Before taking the electron micrographs, the composite dispersed in the distilled water ultrasonically up to 3 min, and then, this dispersed suspension was dropped onto the Cu-grid and observed at 100 Kv.

X-ray powder diffraction diagrams were recorded on an X-ray diffractometer (D8 advance-X) using $Cu - K_\alpha$ (λ=0.154056 nm) and Sol-X detector, and the scan rate was 1° min^{-1} (step: 0.02°; step time: 1.2 s).

Results and discussion

XRD analysis

The XRD patterns of the TiO_2 powder, TiO_2 nanotubes, and $Co(OH)_2$/TiO_2 nanotube composites with different amounts of $Co(OH)_2$ loading on TiO_2 nanotubes were shown in Fig. 1. We can see that the XRD patterns of the TiO_2 powder in Fig. 1(a) correlate with the reported pattern of anatase TiO_2 (JCPDS, card no: 21-1272). According to the XRD patterns of the TiO_2 nanotubes in Fig. 1(b), the raw material nanocrystalline TiO_2 powder converts to anatase TiO_2 nanotubes through the hydrothermal process, but the peaks of anatase TiO_2 became broad. In Fig. 1c–e, the XRD pattern of the $Co(OH)_2$/TiO_2 nanotube composites correlate with the reported pattern of anatase TiO_2 and β-$Co(OH)_2$; the clear and strong diffraction of β-$Co(OH)_2$ peaks at 2θ, corresponding to (001), (100), (101), (102), (110), and (111), respectively. With increasing amounts of $Co(OH)_2$, the major diffraction peaks of $Co(OH)_2$ became more and more obvious, and that of TiO_2 nanotubes, die down gradually.

The morphology of titanium oxide nanotubes

Transmission electron electron microscopy (TEM) of TiO_2 nanotubes and $Co(OH)_2$/TiO_2 nanotube composites are

Fig. 1 XRD pattern of the TiO$_2$ powder (**e**), TiO$_2$ nanotubes (**d**) and Co(OH)$_2$/TiO2 nanotube composites, weight ratios of Co(OH)$_2$/TiO2: **a** 3:1, **b** 1:1, and **c** 1:3
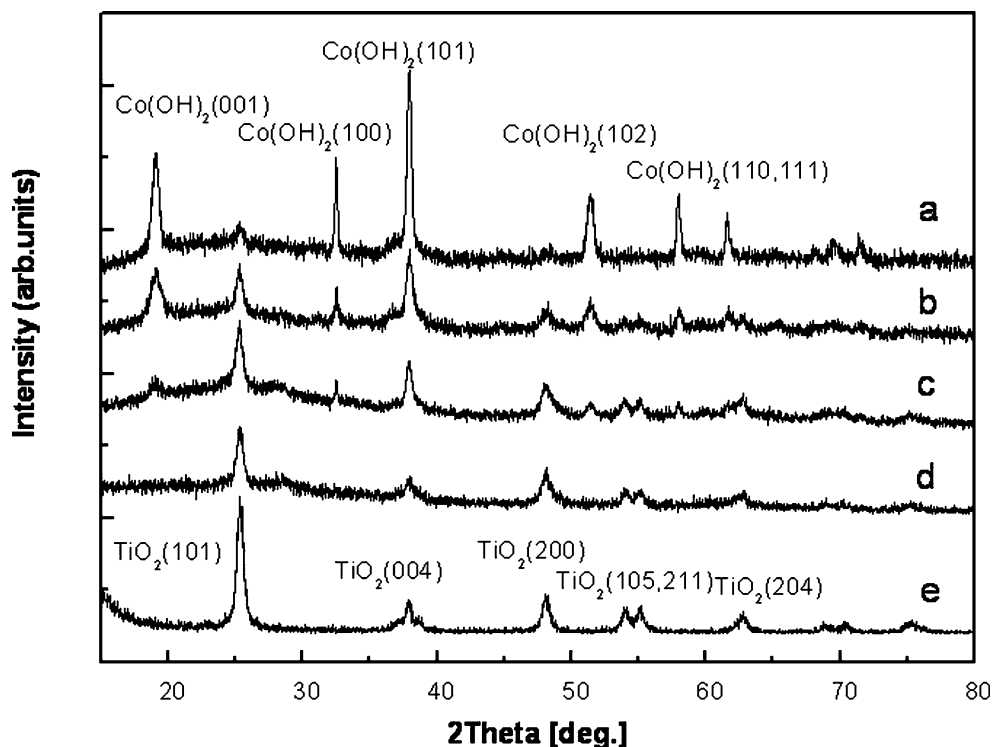

shown in Fig. 2a and b, respectively. We can see that these nanotubes are uniformly straight hollow tubes, of which the diameter is around 10 nm and the length is more than 300 nm. Due to the proper mesoporous network of nanotubes, the easily accessible electrode/electrolyte interface allows a quick charge and discharge process. It is helpful for the electrolyte to come into the inside of composites through the TiO$_2$ nanotubes and access more active materials. In Fig. 2b, the TiO$_2$ nanotubes in Fig. 2a are bundled in the Co(OH)$_2$. It makes Co(OH)$_2$ more dispersed and the electrolyte easier to contact. The Co(OH)$_2$ covers the TiO$_2$ nanotubes tightly. So, partial TiO$_2$ nanotubes that emerge in the composite can be seen clearly, but those bundled in the Co(OH)$_2$ are hard to see distinctly.
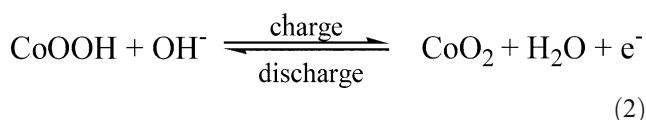
Cyclic voltammetry

Figure 3 shows the cyclic voltammetry (CV) curves of electrodes fabricated from TiO$_2$ nanotubes (curve a) and Co(OH)$_2$/TiO$_2$ nanotube composites (curve b, c, d). Obviously, the extremely low current of curve a suggests that TiO$_2$ nanotubes alone has a very small specific capacitance; it has less contribution to the capacitance of composites. Therefore, the capacitance measured in curve b, c, and d roots in the Co(OH)$_2$ phase of the composite. Two pairs of redox peaks are visible in curve b, c and d, according to the peak currents of p1, p2, p3, and p4, indicating that the capacitance characteristics of the Co(OH)$_2$ phase is distinct

from that of the electrical double-layer capacitance and root on redox capacitance, and the redox peak are primary contributions to the capacitance of composites. Based on the average value of peak potential of p1 vs p3 and p2 vs p4, peaks p1 and p3 may be due to the reaction that follows [23]:

$$\mathrm{Co(OH)_2 + OH^- \underset{discharge}{\overset{charge}{\rightleftharpoons}} CoOOH + H_2O + e^-} \tag{1}$$
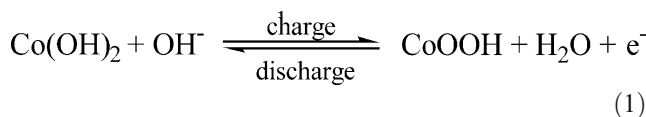
Peaks p2 and p4 may be due to the reaction that follows:

$$\mathrm{CoOOH + OH^- \underset{discharge}{\overset{charge}{\rightleftharpoons}} CoO_2 + H_2O + e^-} \tag{2}$$

It is known that the capacitance of materials is relative to the average current, so according to the currents of curve b, c, and d, we can distinctly see that the capacitance of composites increases with the content of loading Co(OH)$_2$; this is in agreement with the results of galvanostatic charge/discharge.

Electrochemical impedance spectroscopy analysis

Electrical conduction and ion transfer were investigated by electron impedance spectroscopy (EIS) analysis which
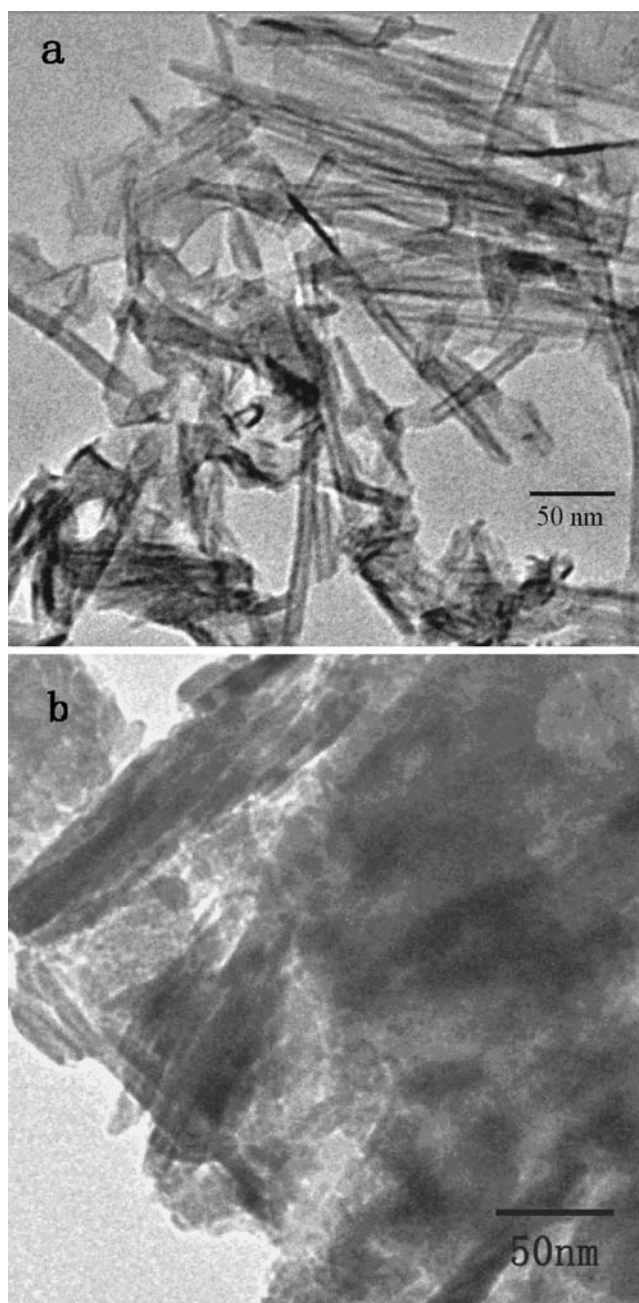
Fig. 3 The CV curves of the electrodes for $Co(OH)_2/TiO2$ nanotubes composites at a scan rate of 10 mV/s in 6 M KOH electrolyte, weight ratios of $Co(OH)_2/TiO2$: **a** 0:1, **b** 1:3, **c** 1:1, and **d** 3:1

characteristics of the composite electrode further controlled by the diffusive resistivity of the electrolyte within the addition of TiO_2 nanotubes. This can be explained as the TiO_2 nanotubes offers a solid support for $Co(OH)_2$, which makes the $Co(OH)_2$ dispersed, and the results are also satisfied in the complicated microcomposite structure. The microstructure can accommodate the electroactive species in the solid bulk electrode material.

Charge–discharge analysis

Figure 5 show the charge–discharge behavior of the composite electrodes between −0.3 and 0.35 V at the current of 2, 5, and 10 mA. The shape of the discharge curve does not show the capacitance characteristics of pure

Fig. 2 TEM images of TiO_2 nanotubes (**a**) and composite (**b**)

could be applied to separate and study electrochemical processes with different time constants. Figure 4 presents the complex–plane impedance plots for the pure $Co(OH)_2$ and $Co(OH)_2/TiO_2$ nanotube composites (the weight ratio of $Co(OH)_2$ and TiO_2 nanotubes is 3:1). The frequency range studied is 10^5 to 10^{-2}. The voltage is kept constant at 0 V during the measurement. At high frequencies, the semicircle is attributable to the charge-transfer process at the composite–electrolyte interface. Here, the charge-transfer resistance of composite and pure $Co(OH)_2$ are almost the same. At low frequency, the slope of curve a is more closer to 45° than that of curve b, which indicates the
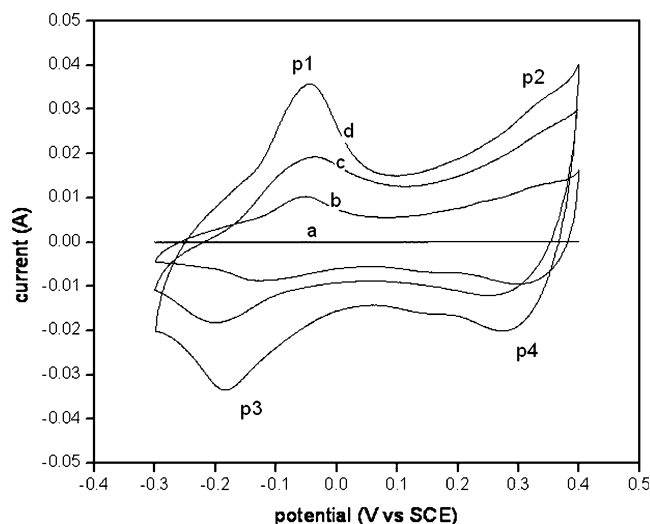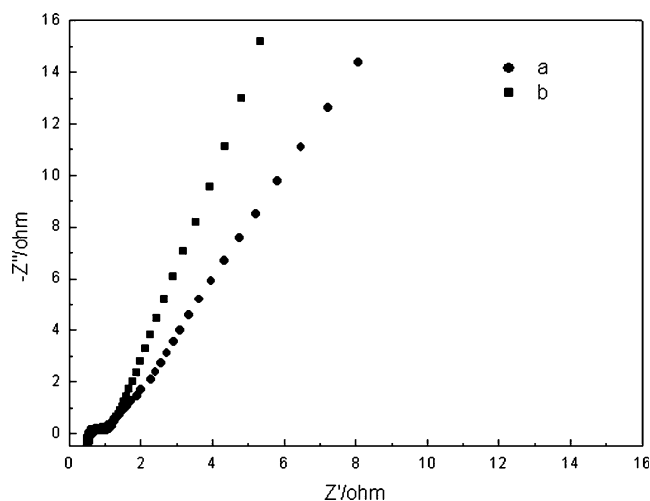

Fig. 4 Impedance Nyquist plots of $Co(OH)_2/TiO_2$ nanotube composites at an applied potential of 0 V in 6 M KOH electrolyte with 50 wt% (**a**) and 0 (**b**) TiO_2 nanotubes
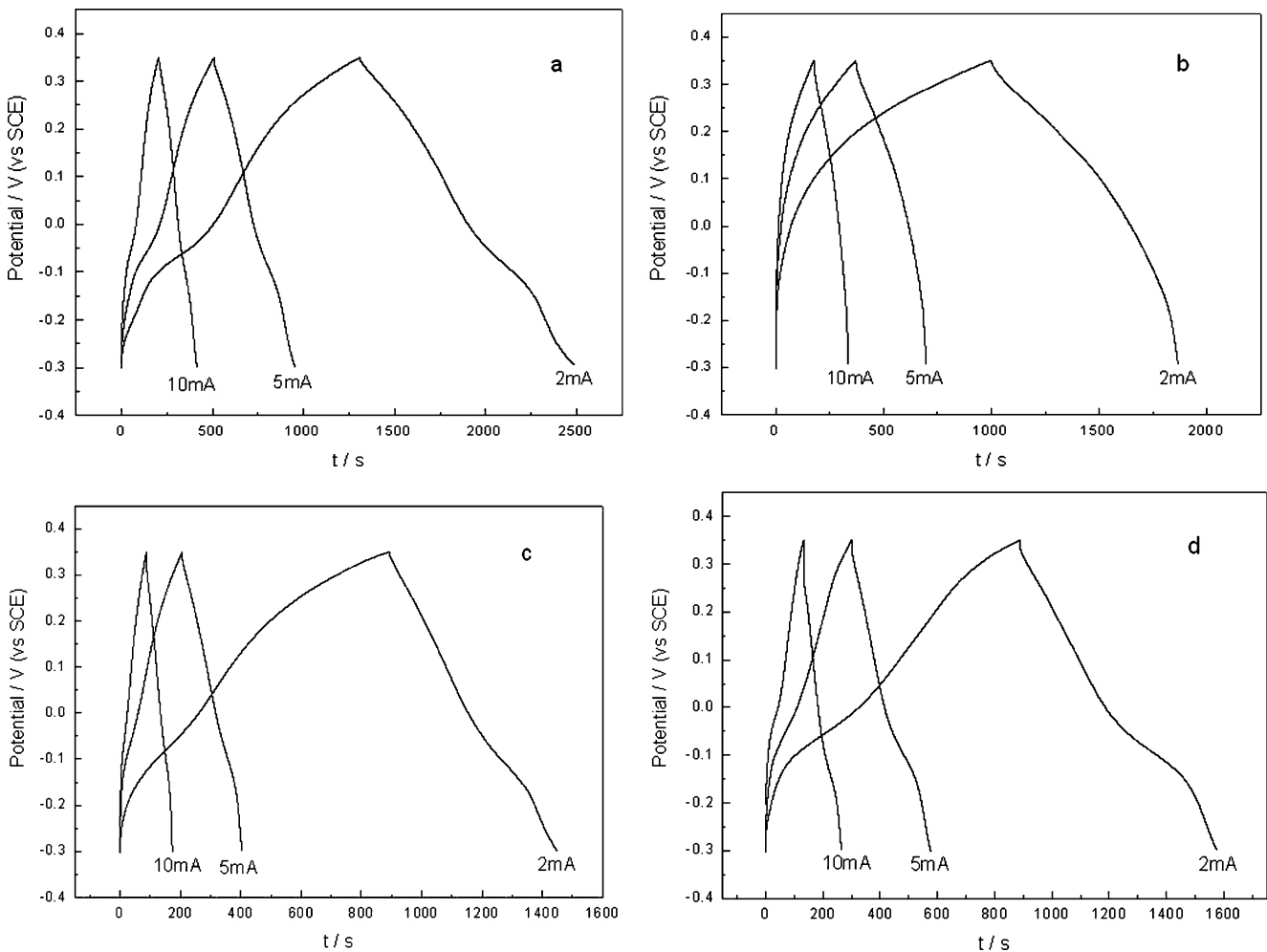
Fig. 5 Charging–discharging behavior of Co(OH)$_2$/TiO$_2$ nanotube composites electrode at a current density of 2, 5, and 10 mA/cm in 6 M KOH electrolyte, weight ratios of Co(OH)$_2$/TiO2: **a** 1:3, **b** 1:1, **c** 3:1, and **d** 1:0

double layer capacitor, in agreement with the result of the curve.

The specific capacitance of the Co(OH)$_2$/TiO$_2$ nanotube composites (C) in the electrode were calculated as follows:

$$C = \frac{I\Delta t}{m\Delta v} \tag{3}$$

with I being the discharge current, m the mass of the composite, Δv the potential window during discharging, Δt the total discharge time, and C the specific capacitance.

The specific capacitance of Co(OH)$_2$ in the composites (C^1) was calculated as follows:

$$C^1 = \frac{C}{a} \tag{4}$$

where a is the weight fraction of Co(OH)$_2$ in the composite.

Based on Eqs. 3 and 4, the specific capacitance of the Co(OH)$_2$/TiO$_2$ nanotube composites and the capacitance of Co(OH)$_2$ in the composite were evaluated; the typical data were shown in Table 1.

According to the CV curves of TiO$_2$ nanotubes, we can see that the TiO$_2$ nanotubes, themselves, have less capacitance; the capacitance of Co(OH)$_2$/TiO$_2$ nanotube composites should result from the pseudocapacitive nature of Co(OH)$_2$. Based on Table 1, with the amounts of Co(OH)$_2$ increasing, the capacitance of Co(OH)$_2$/TiO$_2$ nanotube composites is enhanced gradually, but one of the Co(OH)$_2$ component in the composite is reduced. When the

Table 1 The capacitances of Co(OH)$_2$/TiO$_2$ nanotube composites electrode and the capacitance of Co(OH)$_2$ in the composite evaluated from charge–discharge curves

The weight ratios of TiO$_2$ nanotubes/Co(OH)$_2$	Capacitance (F/g) of the composite in one electrode at 2 mA	Capacitance (F/g) of the Co(OH)$_2$ component in the composite at 2 mA
3:1	106.5	426
1:1	168	336
1:3	229	305
0:1	134	134

weight ratio of Co(OH)$_2$ and TiO$_2$ nanotubes is 3:1, the composite has the maximum specific capacitance of 229 F/g, but the utilization of Co(OH)$_2$ component is not the best. However, when the weight ratio is 1:3, the composite has a poor specific capacitance of 106.5 F/g, but through calculating, the capacitance of the Co(OH)$_2$ component in the composite reach 426 F/g. Nevertheless, it is not right that the more the weight ratio of Co(OH)$_2$ and TiO$_2$ nanotubes is, the better capacitance of the composite is. The capacitance of pure Co(OH)$_2$ is 134 F/g, which is far less than 229 F/g.

Based on the above discussion, we propose that the TiO$_2$ nanotubes play a critical role in optimizing superior capacitive performance of Co(OH)$_2$/TiO$_2$ nanotube composites. The increasing capacitance of Co(OH)$_2$ in the composite means that more Co(OH)$_2$ participates in the electrochemical reaction, the utilization of Co(OH)$_2$ is improved. The capacitance of pure Co(OH)$_2$ being just 134 F/g show the importance of TiO$_2$ nanotubes. We propose that TiO$_2$ nanotubes provide the three-dimensional nanotube network structure for the composite, making the Co(OH)$_2$ more dispersed and improving its utilization. The three-dimensional nanotube network structure can provide more capacious space for the electrochemical reaction; the electrolyte may go inside of composites through the TiO$_2$ nanotubes.

The stability of the active material in 6 M KOH was examined by chronopotentiometry at 2 mA. The result shows approximately 9% loss of capacitance after 1,000 consecutive cycles, implying that a stable Co(OH)$_2$/TiO$_2$ nanotube composite is a practicable electrode material for electrochemical supercapacitors.

Conclusion

In summary, a novel Co(OH)$_2$/TiO$_2$ nanotube composite was successfully prepared. We applied its microstructure for electrochemical supercapacitors, a maximum specific capacitance of 229 F/g was obtained, which was much better than the pure Co(OH)$_2$. The results have proved that TiO$_2$ nanotubes can make the Co(OH)$_2$ more dispersed and

be the active sites for electrochemical reactions, which enhances the utilization of the Co(OH)$_2$. The microstructure can accommodate the electroactive species in the solid bulk electrode material. The Co(OH)$_2$ in the composites is synthesized by normal method. If we load better Co(OH)$_2$ synthesized by special methods on the TiO$_2$ nanotubes, the higher capacitance of composites will be obtained. We can also use this strategy for many kinds of capacitive material. This kind of composites show great potential as the electrochemical supercapacitors.

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