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Supercapacitor electrode with a homogeneously Co_3O_4-coated multiwalled carbon nanotube for a high capacitance

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Abstract

Cobalt oxide (Co_3O_4) was homogeneously coated on multiwalled carbon nanotube through a simple chemical deposition method and employed in supercapacitor electrodes. SEM image indicated the uniform distribution of Co_3O_4 nanoparticles on the surface of the multiwalled carbon nanotube. A maximum specific capacitance of 273 Fg^{-1} was obtained at the charge–discharge current density of 0.5 Ag^{-1}. After 500 cycles of continuous charge–discharge process, about 88% of the initial capacity could be retained.

Keywords: Supercapacitor; Cobalt oxide; Multiwalled carbon nanotube; Charge–discharge

Background

Electrochemical capacitors (ECs) are causing great concern due to their long cycle life and safety tolerance to high-rate charge and discharge [1]. The electrochemical capacitors have higher power density than secondary batteries and higher energy density than conventional capacitors. With the development of nanoscience and technology, nanoscaled cobalt oxide (Co_3O_4) has received great attention for its use in diverse applications such as catalysis, energy storage devices, and electrochemical sensors due to its peculiar properties and controllable morphology compared with the bulk phase [2-4]. In particular, extensive efforts have been devoted to utilize Co_3O_4 for supercapacitors because of its high reversibility and theoretical specific capacitance (3560 Fg^{-1}) [5,6]. Recently, cobalt oxide has been proven to be a potential alternate to expensive RuO_2 which is broadly used as the electrochemically active material in electrochemical capacitors [7-12].

It is well known that Co_3O_4 is an important p-type semiconductor. Co_3O_4 has been used in lithium-ion batteries, heterogeneous catalysis, electrochemical capacitor devices, and other applications. For this purpose, Co_3O_4 has been synthesized using a variety of methods such as sol–gel, reflux, microwave, and hydrothermal methods [13-16]. Furthermore, much work has been done on the controlled synthesis of nanostructure Co_3O_4 and Co_3O_4 cubes, rods, wires, tubes, and sheets [17-21]. Although electrochemical capacitors based on Co_3O_4 have shown excellent electrochemical capacity, its practical application in supercapacitors is still limited in part due to its poor electrical conductivity. In order to improve the electrical conductivity, one of the most common ways is to mix the Co_3O_4 with conductive additives. Introduction of carbon-based composites may be a promising way to improve the electrical conductivity of Co_3O_4. Carbonaceous materials, such as activated carbon, carbon nanotubes (CNTs), and grapheme nanosheets (GNs), can provide matrices for structural stability and fine electron transfer property due to their excellent mechanical flexibility and high electrical conductivity [22-24]. Fu et al. [25] synthesized spherical cobalt oxide nanoparticles along CNTs in supercritical fluid (containing ethanol and CO_2) and studied their electrical transport properties as a Schottky-junction diode. Huang et al. and Tang et al. obtained hybrid MnO_2/carbon nanotube through facile redox and hydrothermal methods, respectively, which both showed high-rate capacitility and fine stability [26,27]. Wang synthesized Co_3O_4@MWCNT composites through a hydrothermal procedure. This hybrid showed

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superior electrochemical performance as a cathode material in aqueous supercapacitors, which gave 590 Fg^{-1} at 15 Ag^{-1} in 0.5 M KOH aqueous solution [28]. Su et al. [29] electrodeposited Co_3O_4 and NiO on the carbon nanotube and obtained a high capacitance of 52.6 mF cm^{-2}.

In this work, we describe a general method to synthesize Co_3O_4/MWCNTs through a simple chemical deposition method. Co_3O_4 nanoparticles can be evenly and tightly attached on the surface of multiwalled carbon nanotubes (MWCNTs), through a long time of constant temperature heating. The obtained samples showed high specific capacitance (273 Fg^{-1} at a current density of 0.5 Ag^{-1}) though just few Co_3O_4 was deposited on the MWCNTs. This method could significantly decrease the consumption of rare cobalt element.

Methods

Materials preparation

MWCNTs (purity, >95%; diameter, 40 to 60 nm; specific surface area, 200 m^2g^{-1}) were purchased from Chengdu Organic Chemicals Co. Ltd., Chengdu, China. All of the other chemicals were of analytical grade and were used as purchased without further purification. Firstly, MWCNTs were acid-treated with concentrated nitric at 140°C for 10 h. The treated MWCNTs were rinsed with distilled water until the PH was 7 and dried at 60°C for 24 h. It is well known that the surface of MWCNTs possesses a great deal of functional carboxyl groups and becomes negatively charged after functioned with nitric acid [30]. This extraordinary change of the tubular structure for MWCNTs was familiar to be coated with inorganic nanomaterials. Secondly, 80 mg of acid-treated MWCNTs was dispersed into 50 ml ethanol by stirring and ultrasonic treatment, then 2.5 ml of 0.5 M $Co(OAC)_2$ aqueous solution was added to the above solution in a state of agitation, followed by the addition of 1 ml of NH_4OH (30% solution) and 1.4 ml of distilled water an hour later. Thirdly, the reaction was kept at 80°C with stirring for 10 h. After that, the reaction mixture was transferred and sealed in a 100-ml Teflon-lined stainless steel autoclave for a hydrothermal reaction at 150°C for 3 h. After cooling to room temperature, the product was collected by centrifugation and rinsed with deionized water and absolute ethyl alcohol in sequence several times until pH was equal to 7, then dried at 80°C for 12 h. The content of Co_3O_4 on the surface of MWCNTs was controlled through the regulation of the $Co(OAC)_2$ content. The $Co(OAC)_2$ contents were controlled to be 0.125, 0.25, 0.5, and 1 mmol. The prepared samples were denoted as Co_3O_4-0.125/MWCNTs, Co_3O_4-0.25/MWCNTs, Co_3O_4-0.5/MWCNTs, and Co_3O_4-1/MWCNTs, accordingly. Pure Co_3O_4 sample was also prepared through the same preparation process as the Co_3O_4/MWCNTs samples.

Structural characterization and electrochemical measurements

The morphology and structure of the samples were characterized by JSM-7001 F field emission scanning electron microscope (FESEM) and DX-2700 X-ray diffractometer (XRD) with a monochromatized Cu K irradiation ($k = 0.154145$ nm), respectively. The composition was characterized by the thermogravimetric (TG) analysis method through Netzsch-STA 449C, from 25°C to 900°C at a heating rate of 10°C min^{-1} in air.

The electrochemical measurements were carried out using a three-electrode system with a 6 M KOH electrolyte in which platinum foils and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. The working electrodes were fabricated by mixing the as-prepared composite, acetylene black, and polytetrafluoroethylene (1% wt.) with a mass ratio of 85:10:5. N-methyl pyrrolidinone (NMP) was also added to form slurry for the spreading on nickel sheets (1.0 cm × 1.0 cm). The working electrodes were pressed at 10 MPa and dried under vacuum at 60°C for 24 h [31]. Cyclic voltammetry (CV) measurement was performed with a CHI660B (Chen Hua Co., Shanghai, China) workstation. The scan rates of CV were in the range from 5 to 100 mVs^{-1}. Electrochemical impedance spectroscopy (EIS) measurement was performed with the electrochemistry workstation IM6 (Zahner Co., Kronach, Germany).

Results and discussion

XRD patterns of the Co_3O_4/MWCNT samples obtained with different cobalt contents are shown in Figure 1. The diffraction peak of the (002) plane for the pure MWCNT sample is sharp. But this peak is gradually weakened with the increasing of $Co(OAC)_2$ content, which indicated that the content of Co_3O_4 increases

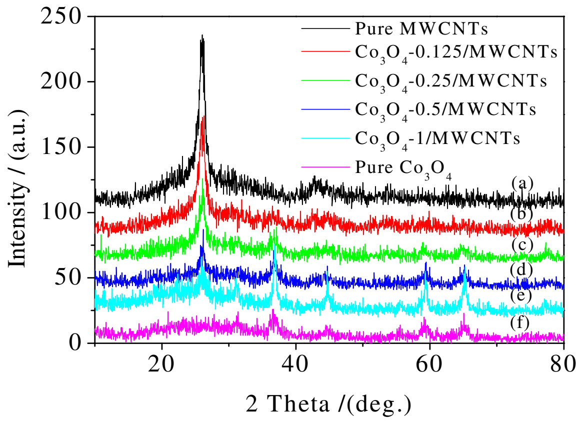

Figure 1 XRD patterns of pure Co_3O_4, pure MWCNTs, and Co_3O_4/MWCNTs with different Co_3O_4 contents. Co_3O_4, cobalt oxide; MWCNT, multiwalled carbon nanotube.

accordingly. When the added $Co(OAC)_2$ content was 0.25 mmol, new diffraction peaks appeared. These diffraction peaks appeared at 18.9, 31.3, 36.8, 44.9, 59.4, and 65.4°. These peaks belong to the characteristic peaks of spinel Co_3O_4, which could be indexed with a JCPDS card (No.43-1003). These diffraction peaks were corresponded to the reflection planes (111), (220), (311), (400), (511), and (440), respectively. These peaks were all in accordance with the pure Co_3O_4 nanomaterial, except the peak at $2\theta = 26°$, which is corresponding to the (002) reflection of the MWCNTs. This indicated that the coated Co_3O_4 on the surface of MWCNTs has the same crystal phase with the pure Co_3O_4 nanoparticles.

To quantify the amount of Co_3O_4 in the composites, TG analysis was carried out in air. The sample was heated from 25°C to 900°C at a rate of 10°C min^{-1}. Figure 2 gives the TG curves for the Co_3O_4/MWCNT hybrid and the pure MWCNT powder. It can be seen that the bare MWCNTs are burned off at around 650°C. On the contrary, the Co_3O_4-0.5/MWCNT hybrid began to lose the weight significantly at around 400°C due to the catalysis of the Co_3O_4 sheath. According to the TG curves, the content of Co_3O_4 can be estimated to be about 35% (wt.%) for the Co_3O_4-0.5/MWCNTs. The Co_3O_4 content of other Co_3O_4/MWCNT samples were also decided to be about 13%, 24%, and 43% (wt.%) for the Co_3O_4-0.125/MWCNTs, Co_3O_4-0.25/MWCNTs, and Co_3O_4-1/MWCNTs, respectively. It can be seen that the content of Co_3O_4 could be handily controlled through this preparation method.

To investigate the surface morphology of Co_3O_4/MWCNT composites, SEM measurement was employed. Figure 3 shows the morphologies of the pure MWCNTs (Figure 3a), pure Co_3O_4 (Figure 3b), and Co_3O_4-0.5/MWCNTs (Figure 3c,d). From Figure 3b, we can see that the as-prepared Co_3O_4 particle is small and homogeneous. But the small particles agglomerate with each other to form large powders, which is inconvenient for contact with the electrolyte during the charging and discharging process. It can be seen from Figure 3a that the pure MWCNTs are smooth and flexible, forming strong intertwined entanglements with a three-dimensional (3-D) network structure. Compared with the pure MWCNTs, the surface of Co_3O_4-particle-coated MWCNTs (Co_3O_4-0.5/MWCNTs) became unsmooth with well-distributed small particles. The particle size is in the range of 5 to 10 nm. The most important thing is that there are no unabsorbed Co_3O_4 particles in the samples. It can be seen that the adopted preparation method is a practical way to coat inorganic nanoparticles on MWCNTs. The MWCNTs could provide a conductive frame network for the Co_3O_4 electrode for electrochemical capacity. On the other hand, coated Co_3O_4 could improve the specific capacity of MWCNT electrode. The SEM spectra of other samples, such as Co_3O_4-0.125/MWCNTs, Co_3O_4-0.25/MWCNTs, and Co_3O_4-1/MWCNTs, are given in the supporting information. It can be seen that the Co_3O_4 particles keep increasing with the addition of $Co(OAC)_2$ (Additional file 1: Figure S1).

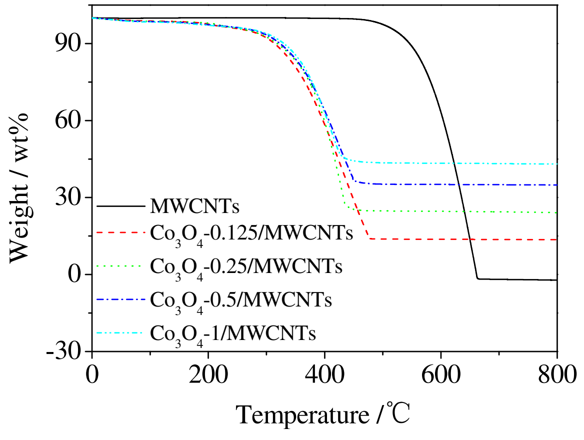

Figure 2 TG curves for the pure MWCNTs and Co_3O_4/MWCNT hybrid. MWCNT, multiwalled carbon nanotube.

In order to evaluate the supercapacitor performance of the electrodes, electrochemical studies were performed using cyclic voltammetry in 6 M KOH aqueous electrolyte. Figure 4a illustrates the CV curves of pure MWCNT electrode at different scan rates in the voltage range of −1 to 0 V. The pure MWCNT electrode has deviated from idealized double layer because of the redox reactions of the functional groups on the surface. The paragraph shows high symmetry between the negative curves and the positive ones, so the MWCNT electrode behaves as a pseudocapacitor. With the increase of the sweep rate, the CV curves have no obvious distortion, indicating a highly reversible system.

Figure 4b shows the cyclic voltammograms of Co_3O_4/MWCNT composites with different Co_3O_4 contents at a scan rate of 50 mV/s between −0.4 and 0.35 V in the 6 M KOH aqueous electrolyte. Compared with the bare MWCNT electrodes, the shapes of the cyclic voltammogram curves in all of the cases are not close to rectangular. The non-rectangular form of the cyclic voltammogram is due to the role of the introduction of Co_3O_4 particles which provide higher pseudocapacitive capacity. It is well known that the capacitive behavior of Co_3O_4 results from the following redox reactions [32]:

$$Co_3O_4 + OH^- + H_2O \leftrightarrow 3CoOOH + e^- \tag{1}$$

$$CoOOH + OH^- \leftrightarrow CoO_2 + H_2O + e^- \tag{2}$$

Compared with the pure MWCNT electrode, the Co_3O_4-coated MWCNT electrodes show significant higher current density in the CV curves. When the content of

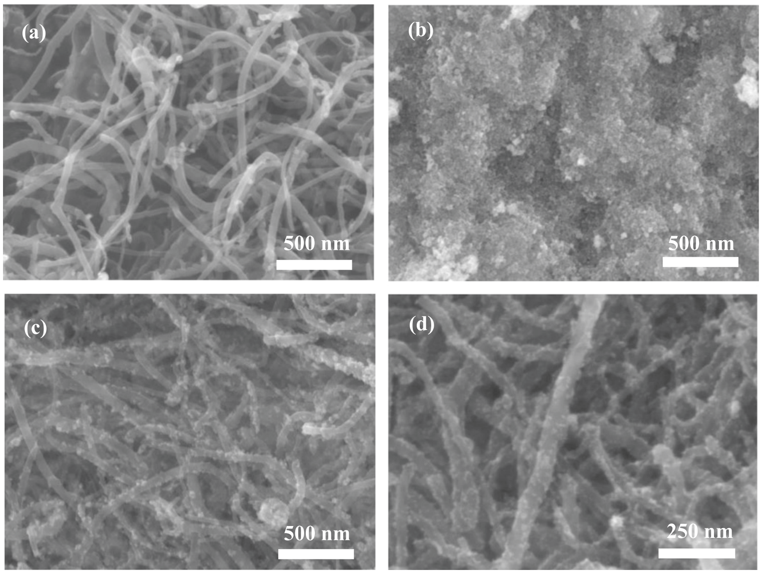

Figure 3 SEM images of **(a)** pure MWCNTs, **(b)** pure Co_3O_4, **(c)** Co_3O_4-0.5/MWCNTs (low magnification), **(d)** Co_3O_4-0.5/MWCNTs (high magnification).

added $Co(OAC)_2$ was 0.5 M, the obtained samples (Co_3O_4-0.5/MWCNTs) give the highest current density which indicated that the Co_3O_4-0.5/MWCNT electrode has the highest specific capacitance. When the content of added $Co(OAC)_2$ solution was increased to 1 mmol (Co_3O_4-1/MWCNTs), the current density decreased abruptly.

The charge–discharge properties of the electrodes were also tested in 6 M KOH aqueous electrolyte. The charge–discharge curves of pure MWCNT, pure Co_3O_4, and Co_3O_4/MWCNT composite electrodes are all shown in Figure 5. The charge–discharge current density is 0.5 Ag^{-1}. Figure 5a shows the charge–discharge curve of pure MWCNT electrode within a potential window of −1 to 0 V. The shape of the curve is closely linear and shows a typical triangle symmetrical distribution indicating a good double layer capacitive property. Figure 5b shows the charge–discharge curve of the pure Co_3O_4 electrode within a potential window of −0.4 to 0.35 V. It can be seen that the curve has significant bend which indicates a pseudocapacitive capacity for the electrodes. Figure 5c shows the charge–discharge of the Co_3O_4/MWCNT composites with different cobalt content in the potential range of −0.4 to 0.35 V. The shape of the charge–discharge curves is similar with that of the pure Co_3O_4 electrode. The average specific capacitances for the electrodes can be calculated on the basis of Equation 3:

$$C = (i \times \Delta t)/(m \times \Delta V) \qquad (3)$$

where C is the specific capacitance (Fg^{-1}), i (A) is the discharge current, $\triangle V$ (V) is the potential window during the discharge process, $\triangle t$ (s) is the discharge time, and m (g) is the mass of electroactive material [33]. The average specific capacitances for the pure MWCNT, pure Co_3O_4, Co_3O_4-0.125/MWCNT, Co_3O_4-0.25/MWCNT, Co_3O_4-0.5/MWCNT, and Co_3O_4-1/MWCNT composite electrodes, which were obtained from charge–discharge

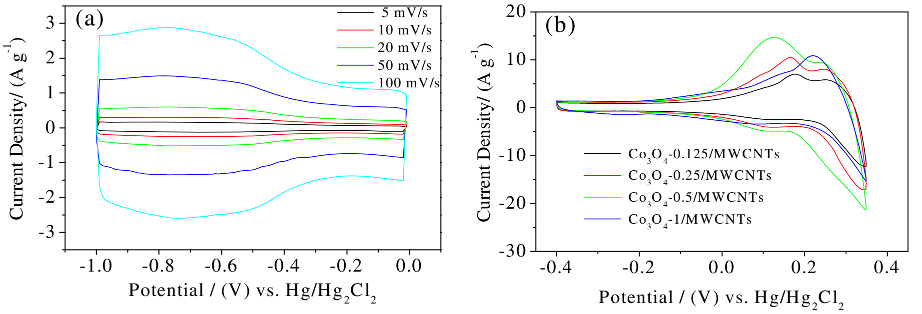

Figure 4 CV curves. CV curves of **(a)** pure MWCNT electrode at different sweep rate, **(b)** Co_3O_4/MWCNT electrode with different Co_3O_4 contents at a sweep rate of 50 mVs^{-1}. Co_3O_4, cobalt oxide; MWCNT, multiwalled carbon nanotube.

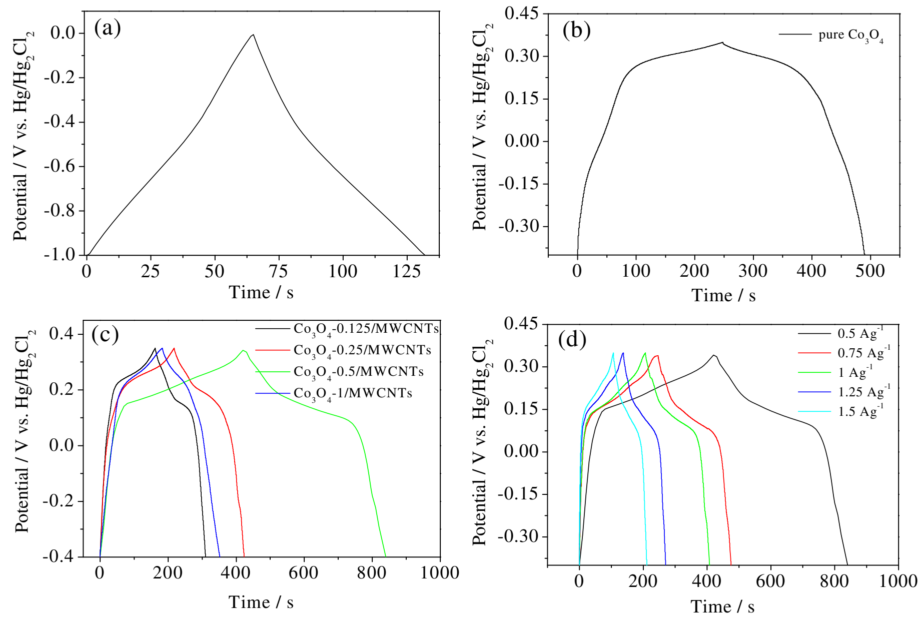

Figure 5 The charge–discharge curves. The charge–discharge curves of the samples **(a)** pure MWCNT electrode at a current of 0.5 Ag^{-1}, **(b)** pure Co_3O_4 electrode at a current of 0.5 Ag^{-1}, **(c)** Co_3O_4/MWCNT electrode with different Co contents at a current density of 0.5 Ag^{-1}, and **(d)** Co_3O_4-0.5/MWCNT electrode at different current density. Co_3O_4, cobalt oxide; MWCNT, multiwalled carbon nanotube.

curves on the basis of Equation 3, were calculated to be about 33, 150, 103, 137, 273, and 118 Fg^{-1}, respectively. The results are identical to that estimated from the cyclic voltammogram curves. This result indicates that it is valuable to combine the high electric conduction of MWCNTs with the large specific capacity of Co_3O_4. Meanwhile, the content of the coated Co_3O_4 should be appropriate.

Figure 5d displays the charge–discharge curves of the Co_3O_4-0.5/MWCNT composite at various current densities in the range of 0.5 to 1.5 Ag^{-1}. The specific capacitances were calculated to be about 273, 160, 134, 88, and 69 Fg^{-1}, respectively. It can be seen that the specific capacitances gradually decreases with the increasing of the discharging current density. This phenomenon might be due to the diffusion limits of the OH^- ion movement.

The electrochemical performance of the electrode was further investigated by the EIS measurements. Figure 6 shows the Nyquist plots of the EIS spectra of pure Co_3O_4 electrode and Co_3O_4-0.5/MWCNT electrode, in the frequency range of 1 Hz to 100 KHz. The obtained EIS spectra are composed of a half semicircle at high frequency and a line at low frequency. The small arc observed at the high frequency is related to the process at the electrode material electrolyte interface (R_{ct}), and the line at the low frequency indicates a capacitive behavior related to the charging mechanism. High-frequency intercepts of the real axis gives the serial resistance (R_s) for the working electrode. It can be seen that the Co_3O_4-0.5/MWCNT has smaller R_{ct} and R_s, indicating a lower electrochemical reaction resistance and electron transfer resistance. Furthermore, the straight line of the Co_3O_4-0.5/MWCNT spectra is more close to 90° compared with the pure Co_3O_4 spectra which shows that the Co_3O_4-0.5/MWCNTs possess a more ideal capacitive behavior.

Figure 7 shows the cycle life of the pure Co_3O_4 and Co_3O_4-0.5/MWCNT electrodes at 0.5 Ag^{-1}. It is clearly seen that the specific capacitance of the Co_3O_4-0.5/MWCNT electrode is much higher than that of pure Co_3O_4 under the same current density. The two electrodes show similar charge–discharge performance in

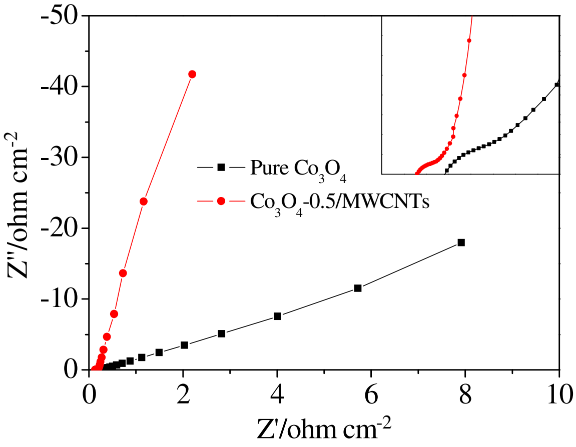

Figure 6 The Nyquist plots of the EIS spectra of Co_3O_4-0.5/MWCNTs and pure Co_3O_4 electrode. Co_3O_4, cobalt oxide; MWCNT, multiwalled carbon nanotube.

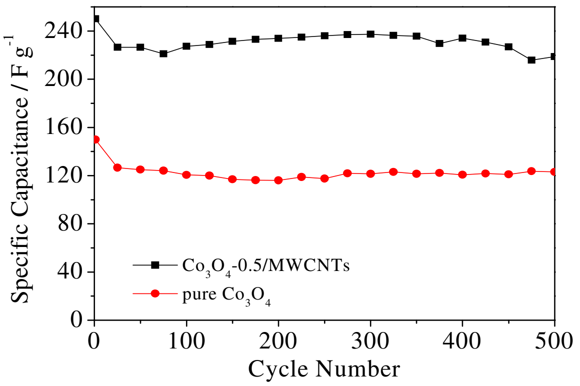

Figure 7 Cycling performances of Co_3O_4-0.5/MWCNTs and pure Co_3O_4 at current density of 0.5 Ag^{-1}. Co_3O_4, cobalt oxide; MWCNT, multiwalled carbon nanotube.

the first 500 cycle times. The process of charging and discharging are both relatively stable. After 500 times charge–discharge, the specific capacity of Co_3O_4-0.5/MWCNT electrodes remains to be about 219 Fg^{-1} which is about 88% of the first discharge capacity.

Conclusions

Co_3O_4 was homogeneously coated on a multiwalled carbon nanotube through a simple chemical deposition method. The contents of Co_3O_4 on the surface of MWCNTs were handily controlled through the regulation of the $Co(OAC)_2$ content. Furthermore, the Co_3O_4 nanoparticles were homogeneously distributed on the surface of multiwalled carbon nanotubes. The coating of Co_3O_4 could significantly increase the specific capacity of MWCNTs. The optimized samples were obtained when the $Co(OAC)_2$ content was 0.5 mmol. The maximum specific capacitance of 273 Fg^{-1} was obtained at the charge–discharge current density of 0.5 Ag^{-1}. After 500 cycles of charge–discharge process, about 88% of the initial capacity could be retained.

Additional file

Additional file 1: SEM images. It can be seen that the Co_3O_4 particles keep increasing with the addition of $Co(OAC)_2$.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

LT carried out the sample synthesis and data analysis and wrote the manuscript. LSJ designed the experiments, analyzed the data, and modified the manuscript. ZBW contributed to the data analysis and manuscript-revising work. WB, NDY, CZ, YY, and WN provided helpful discussion of the experiment. ZWF modified the manuscript. All authors read and approved the final manuscript.

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