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Short Communication

Facilely Synthesized $NiCo_2O_4$/CNTs Nanocomposites for Supercapacitors with Enhanced Performance

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A facile solvothermal method without calcination was successfully developed to prepare $NiCo_2O_4$/CNTs nanocomposites. XRD and TEM images revealed the $NiCo_2O_4$ nanoparticles were tightly bonded on high conductive CNTs surface. The electrochemical properties indicated that the specific capacitance of $NiCo_2O_4$/CNTs was increased 15.4% at 1 A g^{-1}. And 97.1% capacitance of $NiCo_2O_4$/CNTs retained after 3000cycles, which was obviously much higher than that of pure $NiCo_2O_4$ with 81.1% retention.

Keywords: $NiCo_2O_4$; Carbon nanotubes; nanocomposites; supercapacitors

1. INTRODUCTION

Supercapacitors, as a prevailing energy storage device, have been attracting widespread attention due to their high charge-discharge rate and long cycle life [1]. Because of fast and reversible redox reactions, transition metal oxides, such as Fe_3O_4 [2,3], Co_3O_4 [4-6], NiO [7,8], MnO_2 [9], ZnO [10], SnO_2 [11] and V_2O_5 [12] have been widely studied as electrodes for supercapacitors. Especially, binary metal oxides, such as $NiMoO_4$ [13,14], $NiWO_4$ [15], $ZnCo_2O_4$ [16] and $NiCo_2O_4$ [17-20] have been reported to deliver a higher performance than single component oxides due to their feasible oxidation state. Among them, $NiCo_2O_4$ is one of the most promising transition metal oxides for pseudocapacitors owing to nickel occupies the octahedral sites and cobalt distributes over both octahedral and tetrahedral sites, in which the solid-state redox couples Co^{3+}/Co^{2+} and Ni^{3+}/Ni^{2+} are presented [21]. However, pure transition metal oxides always suffer from low conductivity, resulting in unsatisfactory performance [22]. So considerable research efforts about high conductivity carbon materials combined $NiCo_2O_4$ have been devoted to synthesis and characterization, such as

$NiCo_2O_4$/CNTs [23], $NiCo_2O_4$/graphene [24], $NiCo_2O_4$/carbon cloth [25]. F. Cai et al. constructed CNT@$NiCo_2O_4$ core–shell structural nanocable by chemical co-deposition route combined with post-calcination with the capacitance of 1038 F g^{-1} at a current density of 0.5 A g^{-1} [26]. M. Li et al. fabricated $NiCo_2O_4$/CNTs by a one-step chemical bath deposition and annealing method with the capacitance of 930 F g^{-1} at 5 mV s^{-1} [27]. T. H. Ko et al. prepared $NiCo_2O_4$/MWCNTs by a dry synthesis technique and it exhibited a maximum specific capacitance of 822 F g^{-1} [28]. To the best of our knowledge, $NiCo_2O_4$/CNTs nanocomposites has not been synthesized via such a facile solvothermal method without calcination. In this paper, we report the facilely synthesis of $NiCo_2O_4$/CNTs nanocomposites by solvothermal method without calcination. Herein, supercapacitive properties of the synthesized $NiCo_2O_4$/CNTs are enhanced the as an electrode material for supercapacitors. The specific capacitance of $NiCo_2O_4$/CNTs is 938.8 F g^{-1} at a current density of 1 A g^{-1}, which is 15.4% increase compared to the pure $NiCo_2O_4$.

2. EXPERIMENTAL

CNTs used in this study were prepared by CVD method using C_2H_2 as precursor and Fe/Al_2O_3 as catalysts [29]. 1.5 mmol $Ni(NO_3)_2{\cdot}6H_2O$ and 3 mmol $Co(NO_3)_2{\cdot}6H_2O$ were dissolved in 20 ml ethylene diglycol at 80 ℃ (marked as solution A). 9mmol NaOH and 30mg CNTs were dissolved in 40 ml ethylene diglycol at 80 ℃ (marked as solution B). After complete dissolution, solution B was added dropwise into solution A. After vigorous stirring for 30 min, the mixed liquids were implanted into an autoclave. The pressure of autoclave was adjusted to 10 MPa with CO_2. Then the autoclave was performed in an oil bath at 180 ℃, 200 ℃ , 220 ℃ for 8 h. The $NiCo_2O_4$/CNTs were obtained after washing with distilled water and alcohol until the pH reached 7.

The phase structure and morphology of $NiCo_2O_4$/CNTs were characterized by XRD diffractometer (XRD, DX2700) and transmission electron microscope (TEM, JEM-2100). The electrochemical performances of $NiCo_2O_4$/CNTs-based electrodes were measured by a CHI 660E electrochemical workstation using a three-electrode mode in 6 M KOH solution. Platinum foil and Hg/HgO electrodes were used as counter and reference electrodes, respectively. The working electrodes were prepared by mixing each active material (80 wt%) with acetylene black (10 wt%) and polyvinylidene fluoride (PVDF, 10 wt%) in N-methyl-2-pyrrolidone (NMP) to form a slurry. The resultant slurry was pasted onto Ni foam substrate and dried at 120 ℃ for 4 h to remove the solvent. Then, the as-formed electrodes were pressed at 10 MPa. The specific capacitance was calculated according to:

$$C = \frac{i_0 \Delta t}{m \Delta V} \qquad (1).$$

Where i_0, Δt, and ΔV were the discharge current, discharge time, and difference of voltage in the time of Δt during discharge, respectively; m was the mass of $NiCo_2O_4$/CNTs in the electrode.

3. RESULTS AND DISCUSSION

XRD patterns of the CNTs, $NiCo_2O_4$/CNTs and pure $NiCo_2O_4$ (prepared without CNTs by the same procedures) were presented in Fig. 1.

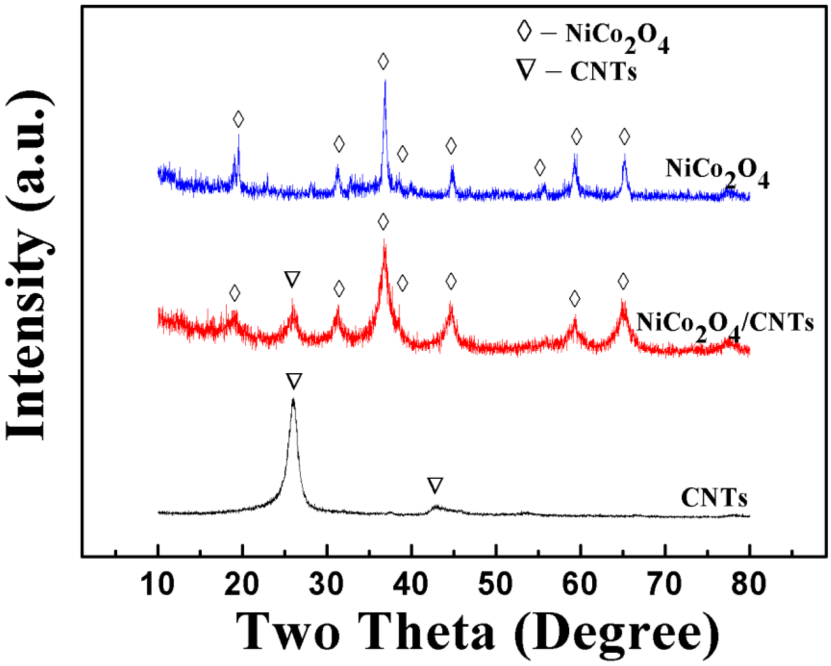

Figure 1. X-ray diffraction of the CNTs, $NiCo_2O_4$/CNTs and pure $NiCo_2O_4$.

The intensity of all peaks was normalized according to the maximum peak. As shown in Fig. 1, nine diffraction peaks of pure $NiCo_2O_4$ were observed at 2θof 18.9°, 31.1°, 36.6°, 38.4 °, 44.6°, 55.5°, 59.1°, 64.9° and 68.3°, with indices of (111), (220), (311), (322), (400), (422), (511), (440) and (531) (JCPDS card No. 20-0781), implying the formation of pure $NiCo_2O_4$ structure obtained by solvothermal method without calcination. The $NiCo_2O_4$/CNTs sample contained two phases with $NiCo_2O_4$ phase (JCPDS card No. 20-0781) and graphite phase (JCPDS card No. 26-1079), indicating that the CNTs were homogeneously surrounded by $NiCo_2O_4$.

The morphology and structure of $NiCo_2O_4$/CNTs nanocomposites were characterized by TEM. Fig. 2 showed the TEM images of the pure CNTs and $NiCo_2O_4$/CNTs (solvothermal temperature of 180 ℃, 200 ℃ , 220 ℃ respectively). Compared with the TEM image of pure CNTs (Fig. 2a), it was evidently observed that $NiCo_2O_4$ nanoparticles (about 10 nm) were effectively coated on CNTs surface. It can be seen from that Fig. 2b, Fig. 2c and Fig. 2d that with the increasing solvothermal temperature, the more $NiCo_2O_4$ nanoparticles were coated on CNTs surface. According to the aforementioned microstructure and morphology characterizations of XRD and TEM, the $NiCo_2O_4$/CNTs nanocomposites were successfully prepared by a facile solvothermal method without calcination.

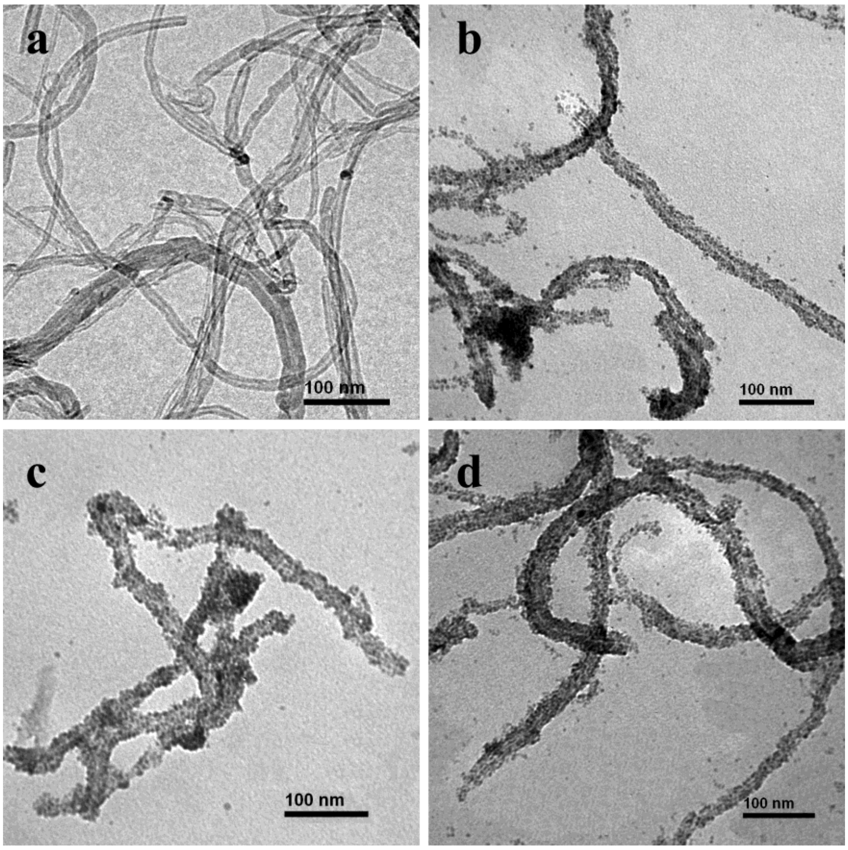

Figure 2. TEM images of (a) CNTs, (b) $NiCo_2O_4$/CNTs (180℃), (c) $NiCo_2O_4$/CNTs (200 ℃), (d) $NiCo_2O_4$/CNTs (220 ℃).

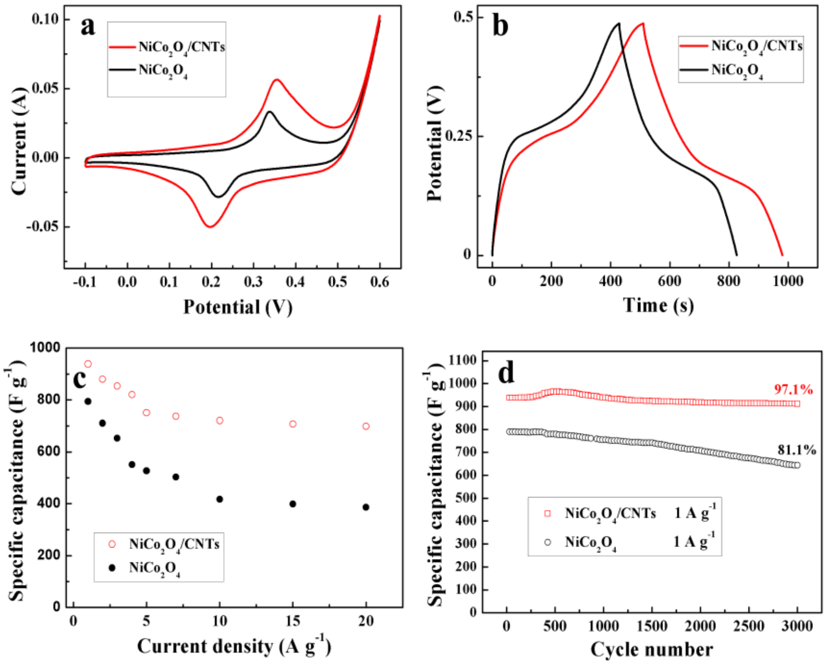

Figure 3. Electrochemical performance of $NiCo_2O_4$/CNTs and pure $NiCo_2O_4$: (a) CV curves. (b) Galvanostatic discharge curves. (c) The specific capacitance at different specific currents. (d) The cycling performances.

Table 1. Comparison of the electrochemical performances of the as-prepared $NiCo_2O_4$/CNTs with the other published results.

Materials	Methods	Specific capacitance (F g^{-1})	Rate performance	Capacity retention	Reference
$NiCo_2O_4$ nanoplates	Hydrothermal and calcination	294 (1 A g^{-1})	48% (10 A g^{-1})	89.8% (2200 cycles)	30
$NiCo_2O_4$ thin-film	Electrochemically	575 (1 A g^{-1})	98% (10 A g^{-1})	99% (1000 cycles)	31
$NiCo_2O_4$ nanoflakes	Chemical bath deposition	490 (15 A g^{-1})	No data	97% (900 cycles)	32
$NiCo_2O_4$ nanorods	Chemical bath deposition	330 (15 A g^{-1})	No data	96% (900 cycles)	32
$NiCo_2O_4$ hexagonal	Hydrothermal and calcination	663 (1 A g^{-1})	88% (8 A g^{-1})	88.4% (5000 cycles)	33
$NiCo_2O_4$	Sol–gel approach	222 (1 A g^{-1})	84% (3.5 A g^{-1})	96.3% (600 cycles)	34
$NiCo_2O_4$–RGO	Self-assembly and thermal treatment	835 (1 A g^{-1})	74% (16 A g^{-1})	108% (4000 cycles)	35
$NiCo_2O_4$ @RGO	Hydrothermal	737 (1 A g^{-1})	50% (10 A g^{-1})	94% (3000 cycles)	36
CNT/ $NiCo_2O_4$	Electrochemical deposition	694 (1 A g^{-1})	82% (20 A g^{-1})	91% (1500 cycles)	23
CNT@ $NiCo_2O_4$	Chemical co-deposition	1038 (0.5A g^{-1})	64% (10 A g^{-1})	100% (1000 cycles)	26
$NiCo_2O_4$ /CNTs	Chemical bath deposition and annealing	940 (5 mV s^{-1})	75% (50 mV s^{-1})	100% (10000 cycles)	27
$NiCo_2O_4$ /MWCNT	Dry synthesis technique	822 (5 mV s^{-1})	No data	88% (1000 cycles)	28
$NiCo_2O_4$ /CNTs	Solvothermal method without calcination	938.8 (1 A g^{-1})	74.4%(20 A g^{-1})	97.1% (3000 cycles)	This work

To compare the electrochemical performance of pure $NiCo_2O_4$ and $NiCo_2O_4$/CNTs nanocomposites, the cyclic voltammetry (CV) and galvanostatic capacitive charge discharge (CD) were tested using a three-electrode mode in a 6 M KOH solution. Fig. 3a showed the CV curves of $NiCo_2O_4$ and $NiCo_2O_4$/CNTs. A pair of redox peaks could be found in each voltammogram, corresponding to the reversible reactions of Co^{3+}/Co^{2+} and Ni^{3+}/Ni^{2+}. The galvanostatic discharge curves of $NiCo_2O_4$ and $NiCo_2O_4$/CNTs at 1 A g^{-1} were shown in Fig. 3b. The potential-time curve of $NiCo_2O_4$/CNTs was more symmetric, indicating not only pseudocapacitive and electrochemical double layer characteristic of $NiCo_2O_4$/CNTs electrode. As shown in Fig. 3c, the specific capacitances of $NiCo_2O_4$/CNTs were calculated to be 938.8, 880.0, 820.8, 720.6, 698.3 F g^{-1} at 1, 2, 4, 10, 20 A g^{-1} , respectively, which were obviously much higher than the specific capacitances of pure $NiCo_2O_4$ (794.4, 710.3, 550.9, 476.8, 436.9 F g^{-1} at 1, 2, 4, 10, 20 A g^{-1} , respectively). The specific capacitance of $NiCo_2O_4$/CNTs was increased 15.4% than the pure $NiCo_2O_4$ at 1 A g^{-1}. In addition, about 74.4% capacitance of $NiCo_2O_4$/CNTs and 54.9% of pure $NiCo_2O_4$ were retained for a 20-time increase in the discharge current density. The cycling performances were also tested at a constant current density of 1 A g^{-1}, as shown in Fig. 3d. The specific capacitance of $NiCo_2O_4$/CNTs was 938.8 F g^{-1} at the first cycle and it gradually decreased to 911.3 after 3000 cycles, with a retention of 97.1%, whereas the specific capacitance of pure $NiCo_2O_4$ decreased from 794.4 F g^{-1} to 644.0 F g^{-1}, with only 81.1% retention. Accordingly, the electrochemical performance of $NiCo_2O_4$/CNTs was enhanced compare to pure $NiCo_2O_4$. It could be owed to the $NiCo_2O_4$ nanoparticles were tightly bonded on high conductive CNTs, which helped facilitate transportation of electrons of supercapacitors. As shown in Table 1, compared to previous reports, such tightly bonded $NiCo_2O_4$/CNTs electrode materials had much better electrochemical performance than other reported $NiCo_2O_4$-based electrode materials, including $NiCo_2O_4$ nanoplates, film, nanoflakes, nanorods, hexagonal, $NiCo_2O_4$–RGO, $NiCo_2O_4$/CNTs and so on (the corresponding results are listed Table 1)[23, 26-28, 30-36].

4. CONCLUSION

In summary, a facile solvothermal method without calcination was successfully developed to prepare $NiCo_2O_4$/CNTs nanocomposites. Due to the $NiCo_2O_4$ nanoparticles were tightly bonded on high conductive CNTs surface, the specific capacitance of $NiCo_2O_4$/CNTs was 938.8 F g^{-1} at 1 A g^{-1}, increasing 15.4% compared to the pure $NiCo_2O_4$. And 97.1% capacitance of $NiCo_2O_4$/CNTs retained after 3000cycles, which was obviously much higher than that of pure $NiCo_2O_4$ with 81.1% retention.

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