Int. J. Electrochem. Sci., 11 **(2016)** 6279 – 6286, doi: 10.20964/2016.07.99

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Synthesis and Electrochemical Measurement of Three Dimensional Carbon Nanofibers/Co_3O_4-Polyaniline Composites as Supercapacitor electrode materials in Neutral Electrolyte

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Received: 21 March 2016 / *Accepted:* 1 May 2016 / *Published:* 4 June 2016

Three dimensional (3D) carbon nanofibers (CNFs) /Co_3O_4-polyaniline (PANI) composites have been successfully prepared by simple hydrothermal reaction and electropolymerization steps. And the electrochemical performances of the composites have been characterized in 1.0 M Na_2SO_4 aqueous solution electrolyte. The CNFs/Co_3O_4-PANI composites exhibited high specific capacitances of 770 F/g at 1A/g and 200 F/g at 20 A/g. Moreover the composites showed excellent cycling stability, their capacitance retained 85.3% at 2 A/g for 1000 cycles. The results showed that the CNFs/Co_3O_4-PANI composites are potential electrode materials for high performance supercapacitors.

Keywords: supercapacitors, carbon nanofibers, polyanline, Co_3O_4

1. INTRODUCTION

Supercapacitors, which also called electrochemical capacitors or ultracapacitors, have drawn great attentions for future energy storage devices because of their long-cycle life, low maintenance costs, safety, higher power density, and fast charge-discharge rate. In principle, there are two energy storage mechanisms for supercapacitors: the electric double layer capacitors (EDLC) and pseudocapacitors [1]. And electrode materials are important components of supercapacitors.

The construction of 3D composites enhance the characteristics of electrodes with large surface area, efficient iron transport and a high number of active sites [2, 3]. In recent years, 3D composites combining pseudocapacitive materials (metal oxides and conducting polymers) with carbonaceous materials (carbon nanotubes (CNTs), graphene and CNFs) have been studied in previous papers [4, 5]. Moreover many 3D Co_3O_4/carbon materials composites, such as Co_3O_4-CNT [6, 7], Co_3O_4/graphene

[8], Co_3O_4/RGO [9], Co_3O_4/CNTs/GNSs [10], CNFs/Co_3O_4 [11], have been demonstrated to improve the specific capacitances to some extent. Although Co_3O_4 has a high theoretical specific capacitance (about 3580 F/g), the reported capacitances of Co_3O_4/carbon electrode materials are still below the theoretical values for the low conductivity and the limited ion diffusion [12]. PANI is a promising carbon coating material for low cost, environmental stability, high conductivity, lightweight, easy synthesis and high capacitance [13]. In our present studies, CNTs and graphene are costly, difficult to fabricate and their discontinuous structures lead to the decrease of electron delivery and ion diffusion [14, 15]. Compared with CNTs and graphene, CNFs have interconnecting networks, strong monolithic form and reasonable electrical conductivity [16]. So, we Choose three dimensional CNFs, which are not only reduce the use of insulated adhesive but also facilitate the diffusion of electrolyte and transport of ion, as substrate.

In this study, we fabricated 3D PANI-Co_3O_4 composites on CNFs by two steps including hydrothermal method and electropolymerization. The CNFs/Co_3O_4-PANI electrode has better specific capacitance of 770 F/g at 1 A/g than CNFs/Co_3O_4 electrode (257.9 F/g at 1 A/g) in 1.0 M Na_2SO_4 aqueous solution electrolyte with a capacitance retention of 85.3% at 2 A/g for 1000 cycles.

2. EXPERIMENTAL

2.1. Fabrication of electrode materials

All the chemical reagents used in the study were of analytical grade (AR). The CNFs ($1\times5cm^2$) used as substrate were washed by ethanol and water several times in ultrasonic bath, and then dried in a vacuum oven at 60 ^oC for 2h.

Synthesis of CNFs/Co_3O_4 composites: firstly, prepared homogeneous solution containing 2 mmol of $Co(NO)_3\cdot6H_2O$, 4 mmol of NH_4F, 10 mmol of urea and 35 ml distilled water. Then the prepared solution was transferred into a 40 ml Teflon-lined stainless steel autoclave and a piece of CNFs was immersed in the solution. The autoclave was sealed and maintained at 100 ℃ for 12 h in an oven. After cooling down to room temperature naturally, the precursor was taken out and washed by ethanol and water several times, dried at 60 ℃ for 2 h. Finally, we obtained Co_3O_4 nanowire arrays on CNFs by heating precursor at 350 ℃ in air for 2 h.

Synthesis of 3D CNFs/Co_3O_4-PANI composites: we obtained the CNFs/Co_3O_4-PANI composites with PANI coating on the surface of CNFs/Co_3O_4 composites by electropolymerization in a solution of 0.05 M aniline and 0.25 M H_2SO_4 with constant voltage of 0.75 V for 5 min. The obtained CNFs/Co_3O_4 composites were used as working electrode. A platinum sheet was used as a counter electrode and SCE was used as the reference electrode.

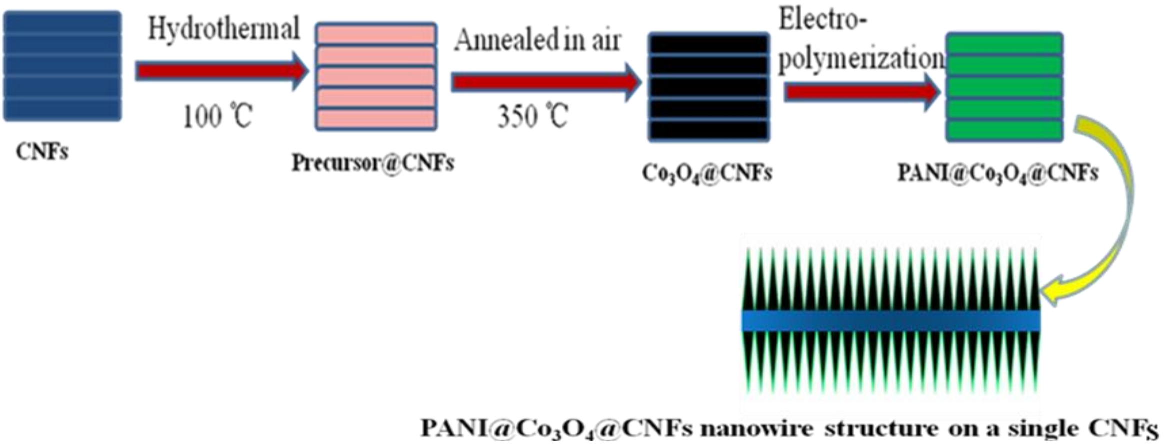
2.2. Materials characterization

The morphologies, microstructures were characterized by field-emission scanning electronmicroscopy (FSEM, Ultra 55) and transmission electron microscopy (TEM, Libra 200FE). The crystal structures were determined by X-ray diffraction (XRD, X'Pert PRO). And the compositions were characterized by Raman spectroscopy (Raman, InVia) and Oxford IE450X-Max80 (EDS, Ultra 55) .

2.3. Electrochemical measurements

The obtained composites acted as working electrodes were measured in a three electrode electrochemical workstation (CHI760c) with the 1.0 M Na_2SO_4 aqueous solution as electrolyte. A platinum sheet was used as the counter electrode. And the reference electrode was SCE. We measured the cyclic voltammometry (CV) and chronopotentiometry to determine the electrochemical performances of composites. The A.C. Impedance was to character impedance, which was conducted in an amplitude of 5 mV at the open-circuit potential with the frequency range between 0.01 Hz and 100 kHz. And the specific capacitance = $I\Delta t/m\Delta V$, where I was chronopotentiometry current, Δt was the time for a full discharge, m indicated the quality of the active material, and ΔV represented the voltage change after a full discharge.

3. RESULTS AND DISCUSSION



Scheme 1. Schematic illustration of the preparation processes of CNFs/Co_3O_4-PANI composites and the Co_3O_4-PANI nanowires structure on a single CNF.

Scheme 1 shows the two preparation processes of 3D CNFs/Co_3O_4-PANI composites, including hydrothermal reaction and electropolymerization. And we obtain core-shell Co_3O_4-PANI nanowires on CNFs substrate. The SEM images of (a) CNFs/Co_3O_4 and (b) CNFs/Co_3O_4-PANI composites with same magnification are shown in figure 1. And the both nanowire arrays are orderly grown on the CNFs with no big micromorphology differences before and after the electrodeposition of PANI. Thus we can know that a thin PANI were coated on the surface of Co_3O_4 nanowires. Figure 1c shows the TEM image of Co_3O_4-PANI core-shell nanostructure. The diameter of Co_3O_4 nanowire is about 75 nm, and the thickness of PANI shell is about 25 nm. Figure 1d shows the EDS of Co_3O_4 and Co_3O_4-PANI nanowire arrays. Comparing the EDS results of Co_3O_4, there are some new elements (C and N) in Co_3O_4-PANI, indicating the coating of PANI on the surface of Co_3O_4 nanowires. These results are in agreement with the results of SEM.

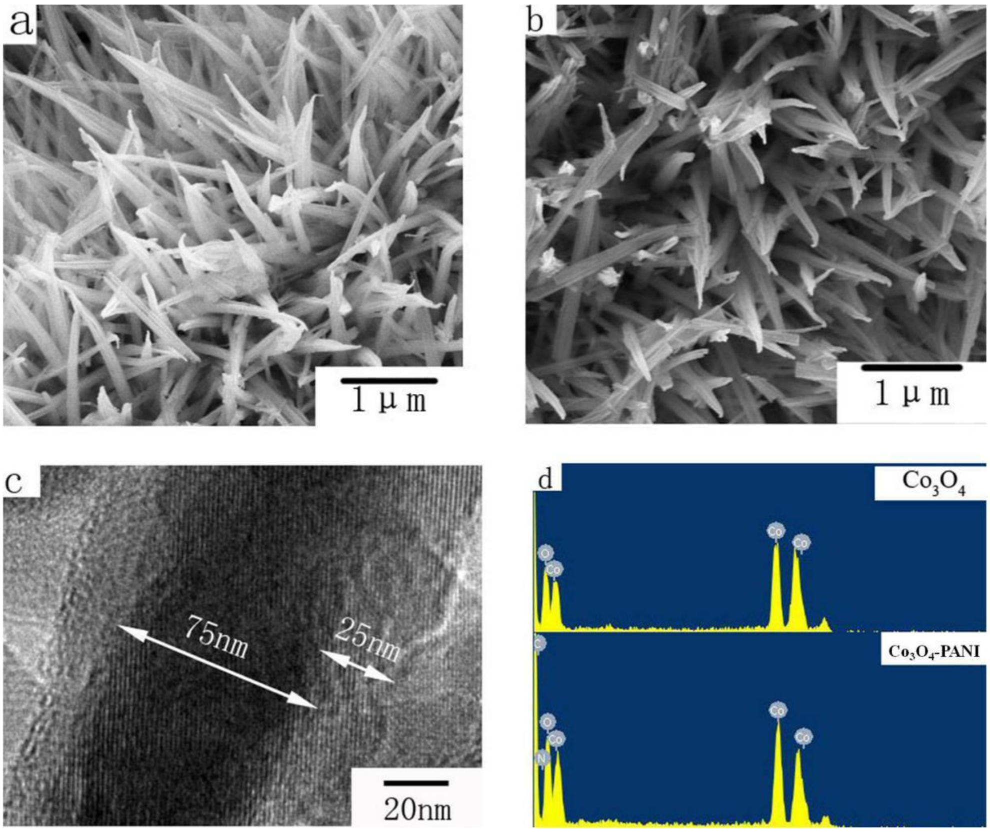
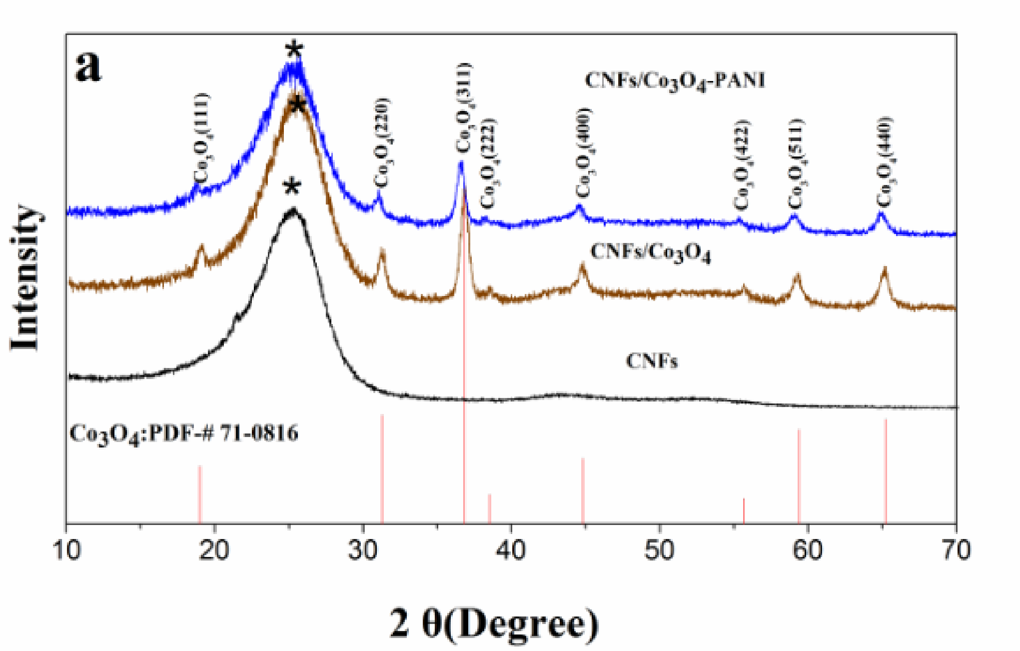


Figure 1. SEM images of (a) CNFs/Co_3O_4 and (b) CNFs/Co_3O_4-PANI composites with same magnification; (c) TEM image; (d) EDS images of Co_3O_4 and Co_3O_4-PANI composites



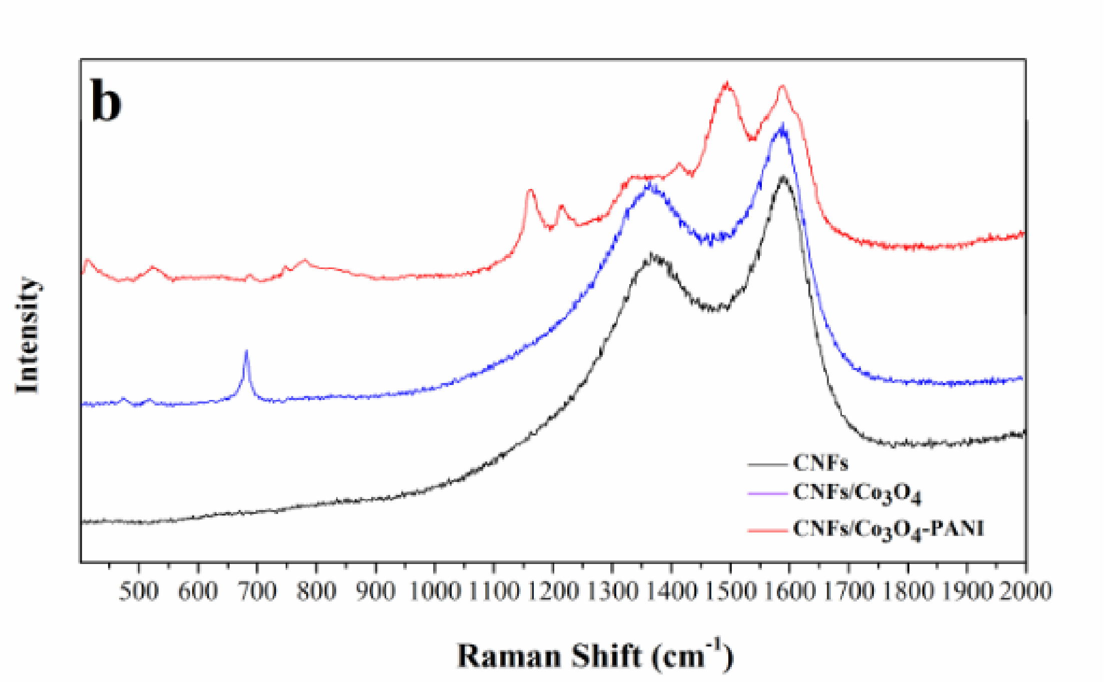


Figure 2. (a) XRD patterns and (b) Raman spectra of the CNFs and the as-prepared composites.

Figure 2a shows the XRD patterns of as-prepared composites. The broad peaks at about 25° (marked with star symbols) are attributed to the amorphous carbon of CNFs substrate. The diffraction peaks at 19.044°, 31.345°, 36.935°, 38.641°, 44.920°, 59.508° and 65.406° can be indexed as the (111), (220), (311), (222), (400), (511) and (440) crystal planes of Co_3O_4, respectively (PDF#71-0816). After the electrodeposition of PANI, the intensity of Co_3O_4 diffraction peaks decrease, which can be attributed to the coated PANI on the surface of Co_3O_4 nanowires. Figure 2b shows the Raman spectra of composites. There are two obvious Raman peaks around 1376 cm^{-1} and 1596 cm^{-1} on both CNFs and CNFs/Co_3O_4 composites, consisting with the D and G bongs of carbon of CNFs. Moreover three additional peaks at 473, 516 and 681 cm^{-1} can be seen on CNFs/Co_3O_4, corresponding to classical vibration modes E_g, F_{2g}, and A_{1g} of Co_3O_4 , respectively [17]. After the electrodeposition of PANI, the intensity of these peaks decrease and some other new peaks appear at 1162 cm^{-1} (C-H bending of quinoid ring), 1413 cm^{-1} (vibrations of C-N$^+$ fragments), 1495cm^{-1} (C=N stretching of the quinoid rings) and 1589 cm^{-1} (C-C stretching of benzene ring) [18, 19].

We study the electrochemical performances of the obtained electrode materials by CV, chronopotentiometry and A.C. Impedance in a three-electrode system with 1.0 M Na_2SO_4 aqueous solution as electrolyte. Figure 3a shows the CV curves at same scan rate of 100 mV/s of CNFs/Co_3O_4 and CNFs/Co_3O_4-PANI electrode. The CV area of CNFs/Co_3O_4-PANI electrode is larger than that of CNFs/Co_3O_4 electrode, indicating that the CNFs/Co_3O_4-PANI electrode shows better capacitance than CNFs/Co_3O_4 electrode. Figure 3b confirms the conclusions by chronopotentiometry curves at the same current density of 1 A/g. Figure 3c displays the summary plots of special capacitances versus different current densities and Figure 3d displays the summary plots of special capacitances versus different scan rates. And the A.C. Impedance curves are shown in figure 3e.

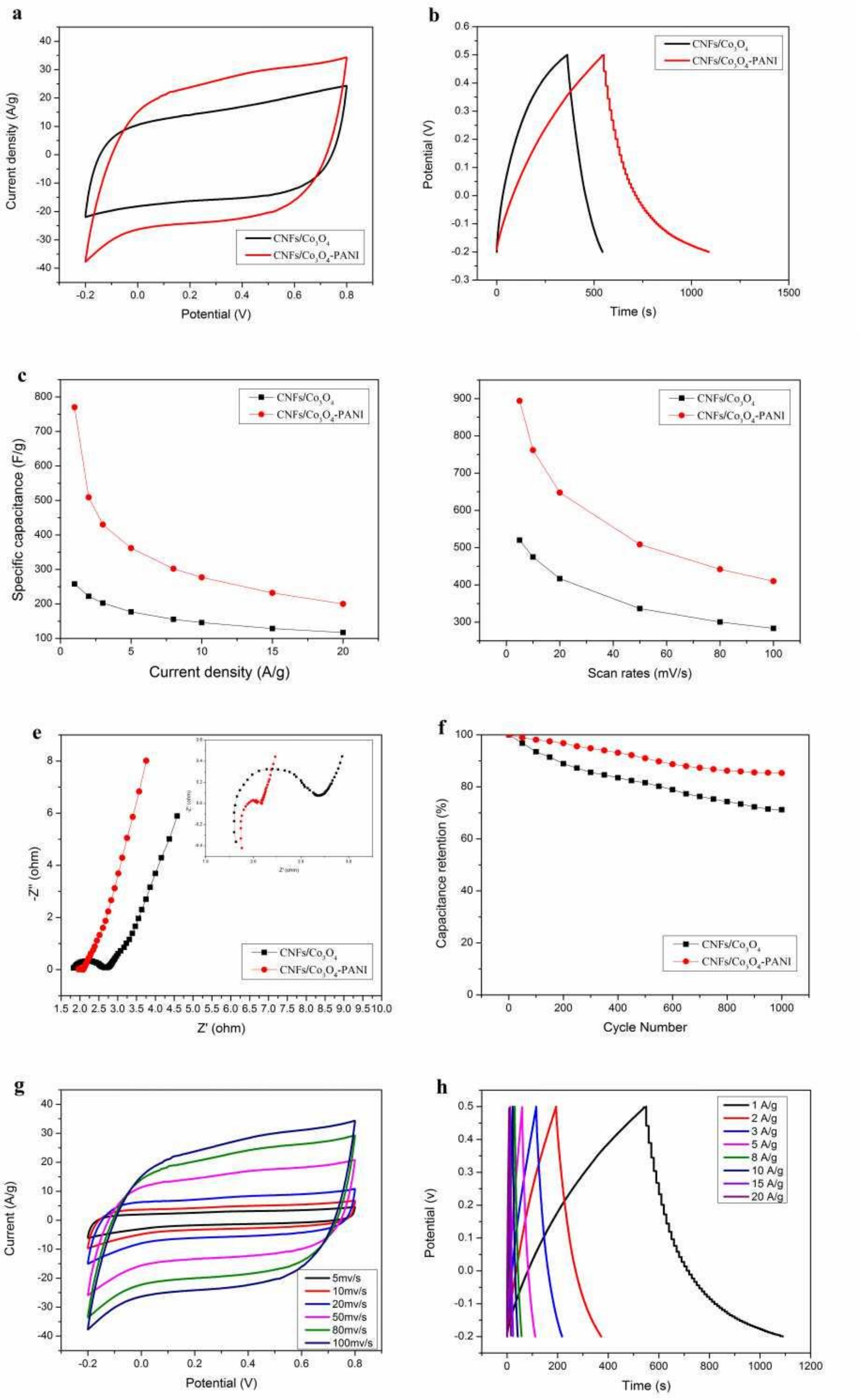


Figure 3. (a) CV curves at 100mv/s; (b) charge-discharge curves at 1A/g; (c) the summary plots of specific capacitances versus different current densities; (d) the summary plots of specific capacitances versus different scan rates; (e) A.C. Impedance curves and (f) cycling performances of CNFs/Co$_3$O$_4$ and CNFs/Co3O4-PANI composites at 2A/g for 1000cycles. (g) CV curves at various scan rates, (h) chronopotentiometry curves at various current densities of CNFs/Co$_3$O$_4$-PANI composites.

The CNFs/Co_3O_4-PANI electrode has much smaller charge transfer resisitance (Rst) than that of CNFs/Co_3O_4 electrode calculated by the diameters of semicircles at high frequency, which suggests the faster charge transfer and transport process. The line slope of the CNFs/Co_3O_4-PANI electrode at low frequency is larger than that of CNFs/Co_3O_4 electrode, which indicates an ideal capacitance performance [20]. Figure 3f shows the cycling performances of the CNFs/Co_3O_4 and CNFs/Co_3O_4-PANI electrodes examined at 2 A/g for 1000 cycles. We can know that the capacitance retention of CNFs/Co_3O_4-PANI electrode is about 85.3 %, but the CNFs/Co_3O_4 electrode is about 71.2 % after 1000 cycles, which attribute to the coated PANI helpful for improving the stability, indicating CNFs/Co_3O_4-PANI composites good cycling stability and potential as electrode materials for supercapacitors. Then figure 3g displays the CV curves of CNFs/Co_3O_4-PANI electrode at various scan rates (5-100 mV/s). With the increase of scan rates from 5 to 100 mV/s, the current densities increase and the basic shapes of CV curves change little as the scan rates increase, indicating good rate capability of composites. The chronopotentiometry curves are shown in figure 3h at various current densities ranging from 1 to 20 A/g, consisting with the results of CV measurements. The chronopotentiometry curves are very symmetrical, indicating reversible electrochemistry. And the specific capacitance of CNFs/Co_3O_4-PANI electrode is 770 F/g at 1A/g. The specific capacitance obtained in the study is higher than that of previous reported electrodes, such as PANI@GNM (452 F/g at 1.0 A/g) [21], PANI@RuO_2 (710 F/g at 5 mv/s) [22], MnO_2@PANI (437 F/g at 1A/g) [23], Co_3O_4@C (205.4 F/g at 0.2A/g) [24], Co_3O_4-CNFs (556 F/g at 1A/g) [25], PANI-coated P-CNFs (366 F/g at 100 mv/s) [26], etc. The enhanced electrochemical performances result from the synergistic effects of PANI and Co_3O_4. Co_3O_4 is a promising electrode material for easily synthesized, low-cost and high theoretical capacitance of 3580 F/g. And PANI is a promising carbon coating material environmental stability, high conductivity and high capacitance [13]. As a result, the coated PANI can enhance the electrical conductivity and ability of CNFs/Co_3O_4-PANI electrode.

4. CONCLUSION

In a word, 3D CNFs/Co_3O_4-PANI composites were synthesized by simple hydrothermal reaction and electropolymerization steps. The nanocomposites exhibited a high specific capacitance of 770 F/g at 1 A/g, excellent cycling stability of a capacitance retention of 85.3% at 2 A/g for 1000 cycles, good electrical conductivity and ion diffusion behavior. These superior electrochemical performances indicate that the 3D CNFs/Co_3O_4-PANI composites could be potential electrode materials for supercapacitors.

ACKNOWLEDGEMENTS
This work was supported by Mianyang City Science and Technology Project (No: 14G-02-5).

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