Facile synthesis of three-dimensional $NiCo_2O_4@Co_3O_4$ nanowire array for application in supercapacitors

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A three-dimensional $NiCo_2O_4@Co_3O_4$ hybrid array on Ni foam electrode for supercapacitors was synthesised via a facile two-step hydrothermal method, in which the $NiCo_2O_4$ was self-assembled on the Co_3O_4 nanowire grown on Ni foam. Moreover, the electrochemical properties of the binder-free electrodes were studied by cyclic voltammograms, galvanostatic charge/discharge tests and electrochemical impedance spectroscopy. Electrochemical characterisations indicated that the unique nano-architecture exhibited excellent electrochemical properties of a high capacitance (1075 F/g), good rate (102.4%), cycling stability (92.6%), which were superior to the pristine Co_3O_4 nanowire. The results clearly confirmed that growing $NiCo_2O_4$ on Co_3O_4 nanowire could substantially improve the capacitive performance of Co_3O_4 materials.

1. Introduction: One-dimensional (1D) metal oxide array as a electrode of electrochemical energy storage has been widely studied because they can provide short diffusion path lengths for ions, leading to high charge/discharge rates [1, 2]. Especially, Co_3O_4 was particularly attractive for application in supercapacitors due to its low cost, as well as low environmental footprint, great redox activity and extremely high theoretical specific capacitance (ca. 3560 F/g). Previous works have indicated that the Co_3O_4 nanowire array grown on Ni foam was higher electrochemical performance comparing to the Co_3O_4 powder [3, 4]. Recently, other materials could be used as a shell structure to modify the Co_3O_4 nanowire array for further improving its performance, such as MnO_2, ZnO and $NiMoO_4$ [5–7]. However, these modified materials suffered low specific capacitance and electrical conductivity, which also limited their further improvement of performance. Spinel nickel cobaltite ($NiCo_2O_4$) as electrode material of supercapacitor has attracted lots of interests due to electrical conductivity and high specific capacitance [8–10]. However, up to now, few $NiCo_2O_4$ modified Co_3O_4 nanowire array grown on Ni foam was reported for application in supercapacitors.

Herein, we report a cost-effective and simple strategy to design and fabricate novel 3D hierarchical $NiCo_2O_4@Co_3O_4$ composite array directly grown on Ni foam. The 3D hierarchical $NiCo_2O_4@Co_3O_4$ array was further investigated as anode material of supercapacitors, which exhibited excellent electrochemical performance, such as good rate and long-term cycle stability in contrast to that of Co_3O_4 individual component. It was expected to have a promising application on energy storage field.

2. Experimental section

2.1. Preparation of $NiCo_2O_4@Co_3O_4$ array on Ni foam ($NiCo_2O_4@Co_3O_4$/NF): First, the Co_3O_4 array on Ni foam (Co_3O_4/NF) was fabricated according to the previous work [3]. Second, 0.29 g $Ni(NO_3)_2{\cdot}6H_2O$, 0.58 g $Co(NO_3)_2{\cdot}6H_2O$ and 1.45 g urea were dissolved in the mixed solution (30 ml deionised water and 30 ml ethanol). Afterwards, the mixed solution and the Co_3O_4/NF were transferred to 80 ml Teflon-lined stainless-steel autoclave and maintained at 130°C for 2 h and cooled down to room temperature, followed by drying at 80°C for 6 h, then calcined at 300°C in air for 2 h. The active mass of $NiCo_2O_4@Co_3O_4$ was measured to be about 0.79 mg/cm^2 by weight difference before and after the reaction.

2.2. Characterisation: Microstructure of the products was examined by X-ray diffraction (XRD; Bruker D8 ADVANCE) with Cu Ka radiation and scanning electron microscopy (SEM; Su-4700, HITACHI Japan) equipped with an energy-dispersive X-ray spectroscopy (EDS) system.

2.3. Electrochemical measurements: Electrochemical tests were carried out on a CHI660E electrochemical workstation (Shanghai) and NEWARE BTS battery tester in the 6M KOH aqueous electrolyte with a three-electrode configuration. A platinum plate and saturated calomel electrode were used as counter and reference electrode, respectively. The $NiCo_2O_4@Co_3O_4$/NF or Co_3O_4/NF electrode (~1 cm × 1 cm) was directly employed as the working electrode.

3. Results and discussion: Fig. 1*A* clearly showed three sharp peaks at 44.4°, 51.8° and 76.3°, corresponding to the diffractions of (111), (200) and (220) planes of Ni, respectively [8]. In addition, other new diffraction peaks at 31.4°, 36.8°, 59.2° and 65° were assigned to (220), (311), (511) and (440) planes of Co_3O_4 phase [4]. As shown in Fig. 1*A*, excluding the diffraction peaks of Ni foam and Co_3O_4, some new diffraction peaks of 43.6°, 63.3° and 75.6° are presented corresponding to (400), (440) and (533) of $NiCo_2O_4$ (JCPDS Card No. 73-1702) [11]. These results indicated the formation of $NiCo_2O_4@Co_3O_4$/NF. Fig. 1*B* shows the EDS analysis of $NiCo_2O_4@Co_3O_4$ grown on NF, in which Ni, Co, and O elements were observed. Furthermore, the molar ratio of Ni:Co:O was about 1.0:3.3:5.8, in which the mass ratio of Co_3O_4 in $NiCo_2O_4@Co_3O_4$ was calculated to be about 31.0 wt%. It further indicated the formation of $NiCo_2O_4$ and Co_3O_4 grown on Ni foam. Figs. 1*C* and *D* obviously showed different structure of Co_3O_4/NF and $NiCo_2O_4@Co_3O_4$/NF, respectively. The Co_3O_4 nanowire array was uniformly grown on the backbones of Ni foam with diameter of 105.0 nm. After introduction of $NiCo_2O_4$, the thin and dense layer of nanowire array was uniformly coated on the backbones

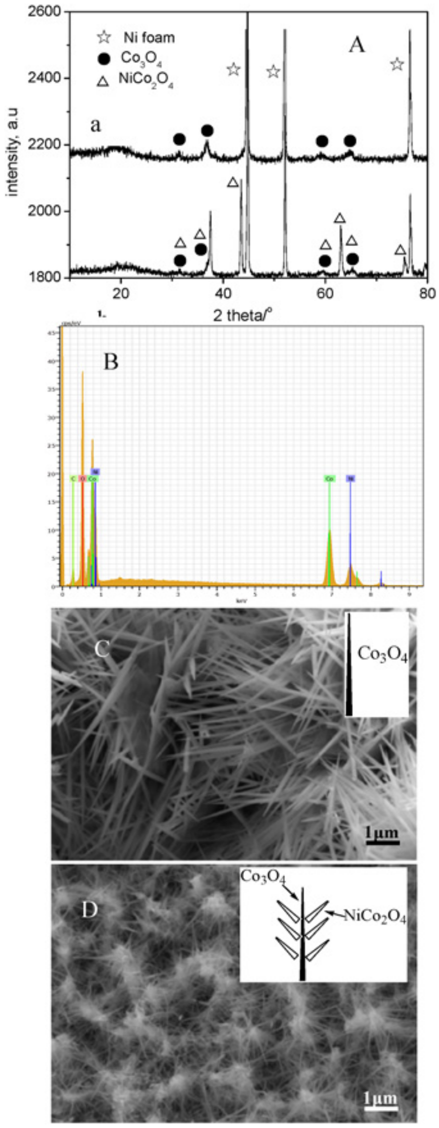

Fig. 1
A XRD pattern of (a) Co_3O_4/NF and (b) $NiCo_2O_4$@Co_3O_4/NF
B EDS pattern of Co_3O_4@$NiCo_2O_4$/NF
C SEM image of Co_3O_4/NF
D SEM image of $NiCo_2O_4$@Co_3O_4/NF. The inset of (C) and (D) was the schematic structure of corresponding samples

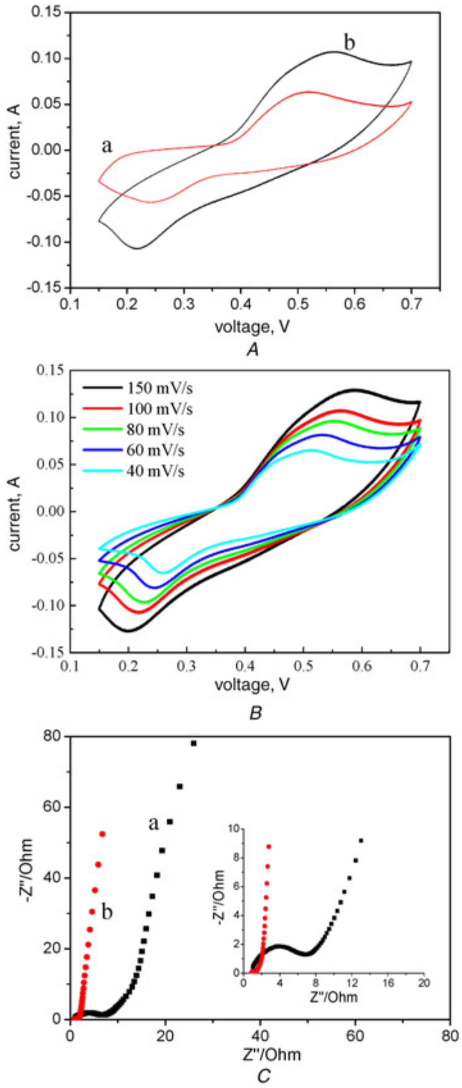

Fig. 2
A CV curves of (a) Co_3O_4/NF and (b) $NiCo_2O_4$@Co_3O_4/NF
B CV curves of $NiCo_2O_4$@Co_3O_4/NF at different scan rate
C Impedance Nyquist plots of (a) Co_3O_4/NF and (b) $NiCo_2O_4$@Co_3O_4/NF at open circuit potential

of the Ni foam as shown in Fig. 1*D*. The uniform array structure was still well retained even after the $NiCo_2O_4$ nanowires were decorated on the Co_3O_4 side (in the inset of Fig. 1*D*). The nanowire tended to interconnect with each other, affording a 3D array structure. These unique features would undoubtedly increase the surface area of active materials, ultimately improving its electrochemical properties.

The cyclic voltammogram (CV) curves of the Co_3O_4/NF and $NiCo_2O_4$@Co_3O_4/NF were compared as shown in Fig. 2*A*. All samples showed similar CV curves, in which a couple of redox peaks was clearly observed. The result indicated the faradaic capacitive behaviour of all samples [10]. It was also noted that the CV area of $NiCo_2O_4$@Co_3O_4/NF was larger comparing to Co_3O_4/NF, indicating the improvement of Co_3O_4/NF' electrochemical performance after the introduction of $NiCo_2O_4$. Fig. 2*B* shows the CV curves of the $NiCo_2O_4$@Co_3O_4/NF electrode in 6M KOH aqueous electrolyte at various scan rates ranging from 40.0 to 150.0 mV/s. All the curves in the plot presented a highly similar characteristic. Even in a rapid scan rate as 150.0 mV/s, the curve still revealed the distinct redox peaks, indicating a high-rate charge–discharge ability [12]. Fig. 3*C* shows the impedance Nyquist plots of the Co_3O_4/NF and $NiCo_2O_4$@Co_3O_4/NF in the frequency range of 0.01–100 kHz. The charge transfer resistance of Co_3O_4/NF and $NiCo_2O_4$@Co_3O_4/NF was estimated to be 0.8 and 0.7 Ω, respectively. The smaller charge transfer resistance of the $NiCo_2O_4$@Co_3O_4/NF was attributed to the $NiCo_2O_4$ nanowire direct grafted onto the Co_3O_4 nanowire, indicating high electronic conductivity. In a low-frequency area, the $NiCo_2O_4$@Co_3O_4/NF has a more ideal straight line, indicating more efficient electrolyte and proton diffusion [9].

The galvanostatic charge/discharge (GCD) curves of Co_3O_4/NF and $NiCo_2O_4$@Co_3O_4/NF were compared as shown in Fig. 3*A*. It could be seen that both charge and discharge times of the $NiCo_2O_4$@Co_3O_4/NF were much longer comparing to Co_3O_4/NF. The specific capacitance of Co_3O_4/NF and Co_3O_4@$NiCo_2O_4$/NF were about 945 and 1075 F/g, respectively. In a comparison, the specific capacitance of Co_3O_4@$NiCo_2O_4$/NF was obviously higher than that of Co_3O_4@ZnO (e.g. 857.7 F/g) and Co_3O_4@MnO_2 (e.g. 560.0 F/g) [5, 7]. Fig. 3*B* shows the electrochemical capacitance of the Co_3O_4/NF and $NiCo_2O_4$@Co_3O_4/NF at various discharge current densities. It showed that when the current was improved from 2.0 to 10.0 A/g, the specific capacitance

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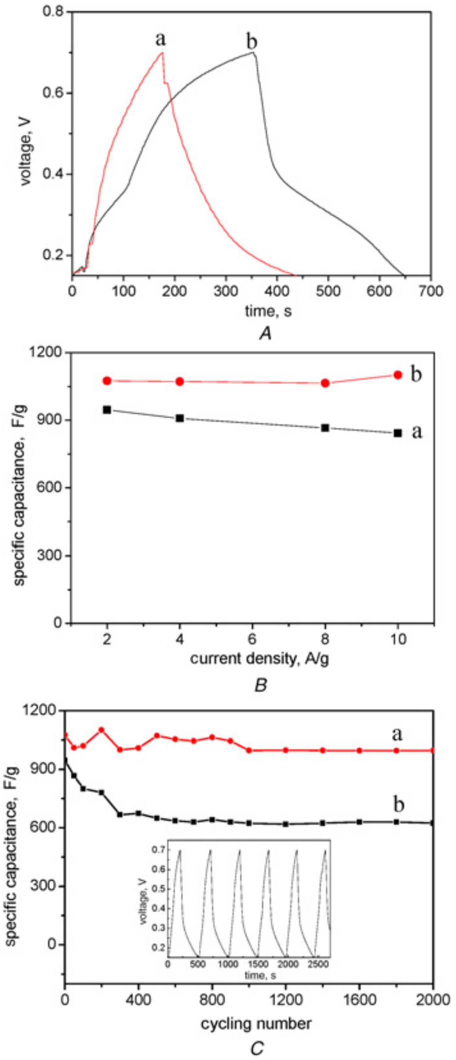

Fig. 3
A GCD curves of (a) Co_3O_4/NF and (b) $NiCo_2O_4$@Co_3O_4/NF at a current of 2 A/g
B Specific capacitance of (a) Co_3O_4/NF and (b) $NiCo_2O_4$@Co_3O_4/NF at various current densities
C Cycling performance at the current density of 2 A/g

of Co_3O_4/NF and $NiCo_2O_4$@Co_3O_4/NF electrode maintained its 89.1 and 102.4%, respectively. The reason was that the ions in the electrolyte were believed to diffuse almost fully into the holes of the electrode at low scan rate, while a higher capacitance of $NiCo_2O_4$@Co_3O_4/NF was observed at high scan rate because of the strong contact between the ions and the $NiCo_2O_4$@Co_3O_4 active materials [12]. The long cycle life of Co_3O_4/NF and $NiCo_2O_4$@Co_3O_4/NF was further investigated at a current density of 2 A/g for 2000 cycles as shown in Fig. 3*C*. As expected, the $NiCo_2O_4$@Co_3O_4/NF showed the higher specific capacitance for 2000 cycles comparing to the Co_3O_4/NF. Impressively, the specific capacitance of the Co_3O_4/NF and $NiCo_2O_4$@Co_3O_4/NF electrode was about 66.0 and 92.6% retention, respectively. The long cycle life was attributed to the hierarchical nanostructure with pores and good adhesion between the hierarchical $NiCo_2O_4$@Co_3O_4 array and Ni foam, resulting in good stability of structure during the galvanostatic charge–discharge process [12].

4. Conclusion: In summary, a 3D $NiCo_2O_4$@Co_3O_4 hybrid array on Ni foam was synthesised via a facile two-step hydrothermal method. The hybrid electrode exhibited better rate performance and cycling stability comparing to Co_3O_4 array. This work provided a possibility of constructing advanced electrodes with high specific capacitance, excellent rate capability and cycling stability for high-performance electrochemical capacitors. More importantly, the electrode design concept could be easily generalised to other binary or ternary metal oxides with unique microstructures or application in electrode of electrochemical energy storage.

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6 References

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