SCIENTIFIC REPORTS

OPEN

Chemical insights into the roles of nanowire cores on the growth and supercapacitor performances of Ni-Co-O/Ni(OH)₂ core/shell electrodes

Received: 04 November 2015

Accepted: 22 January 2016

Published: 09 February 2016

Xuesong Yin^{1,*}, Chunhua Tang^{1,*}, Liuyang Zhang¹, Zhi Gen Yu² & Hao Gong¹

Nanostructured core/shell electrodes have been experimentally demonstrated promising for high-performance electrochemical energy storage devices. However, chemical insights into the significant roles of nanowire cores on the growth of shells and their supercapacitor behaviors still remain as a research shortfall. In this work, by substituting 1/3 cobalt in the Co₃O₄ nanowire core with nickel, a 61% enhancement of the specific mass-loading of the Ni(OH)₂ shell, a tremendous 93% increase of the volumetric capacitance and a superior cyclability were achieved in a novel NiCo₂O₄/Ni(OH)₂ core/shell electrode in contrast to a Co₃O₄/Ni(OH)₂ one. A comparative study suggested that not only the growth of Ni(OH)₂ shells but also the contribution of cores were attributed to the overall performances. Importantly, their chemical origins were revealed through a theoretical simulation of the core/shell interfacial energy changes. Besides, asymmetric supercapacitor devices and applications were also explored. The scientific clues and practical potentials obtained in this work are helpful for the design and analysis of alternative core/shell electrode materials.

Electric energy storage devices with both large energy capacity (energy density) and fast charging ability (power density) are highly demanded nowadays in numerous applications^{1–3}. Traditional capacitors principally employ fast static electric storage but exhibit relatively low energy density, and batteries normally involve slow electrode reactions to realize relatively high energy densities^{4,5}. As a bridge between capacitors and batteries, electrochemical capacitors, also known as supercapacitors, have shown great potentials to balance energy density and power density by combining fast surface-tended electrochemical reactions and static electric storage^{6,7}. Currently, most commercial supercapacitors utilize carbon-based materials, due to their large specific areas, low costs and compatibility with various electrolytes^{8–10}. Categorized as electrochemical double layer capacitors (EDLCs), the specific capacitances of carbon based supercapacitors are limited by their less electrochemically active nature^{8,11}. To achieve higher capacitances, electrochemically active electrode materials are developed for supercapacitors, known as pseudo-capacitors^{6,7,12}. Nano-structured transition metal oxides/hydroxides, such as RuO₂, MnO₂, MoO₃, CoO_x/(OH)_x and NiO_x/(OH)_x, become very attractive candidates due to their multiple electronic states and flexibility of morphological manipulation^{13–23}. Among them, Ni(OH)₂ is one of the most outstanding candidates because of its high gravimetric capacitance, low-cost, non-toxicity and easy accessibility to nanostructures^{20,24,25}.

Although experimental gravimetric capacitances of Ni(OH)₂ close to its theoretical value were achieved in literature, the small loadings limit their applications as real capacitor devices^{26,27}. Especially, the difficulty in growing high loading of active material on substrates leads to a small total capacitance in a unit volume or areal, which reduces the practical significance of these electrodes to a great extent²⁸. Practically, 3D Ni foams (NF) have been applied as the substrate due to their relatively high surface area, conductivity and corrosion resistance to alkaline electrolyte for Ni(OH)₂ based supercapacitor. Despite its much enlarged surface area than a flat substrate, there is still a very high percentage of unused pore space within the Ni foam attributed to its relatively large pore size. Therefore nanowire cores were grown on nickel foams prior to the growth of active material to form core/shell structure that extends into the previously unused pore space. This approach can make more pore space usable

¹Department of Materials Science and Engineering, National University of Singapore, 117576, Singapore. ²Institute of High Performance Computing, 1 Fusionopolis Way, Singapore 138632, Singapore. *These authors contributed equally to this work. Correspondence and requests for materials should be addressed to H.G. (email: msegongh@nus.edu.sg)

Figure 1. SEM images of (a) Co₃O₄ and (b) NiCo₂O₄ nanowires with magnified images in their insets, and (a') Co₃O₄/Ni(OH)₂ and (b') NiCo₂O₄/Ni(OH)₂ core/shell structures on NF with their photos in the insets.

in NF and the loading of active material can be dramatically increased as the available surface area is greatly enlarged for the deposition of active materials. Various materials, such as carbon-based nanomaterials^{29–34}, TiN³⁵, TiO₂³⁶, FeO_x³⁷, NiS_x³⁸, Ni³⁹, (Ni,Co)O_x/(OH)_x^{39–41}, have been employed as cores for Ni(OH)₂ shell growth. The Ni, Co oxides based cores are of great interests, because they not just serve as an agent to increase the surface area but also contribute to the total capacitance owing to their own high electrochemical activities^{40,42–49}. Tang *et al.* reported a Co₃O₄ nanowires/Ni(OH)₂ core/shell hybrid on nickel foam electrode and achieved a specific capacitance around 15 Fcm^{−2} at a current of 5 mAcm^{−2}⁴¹. NiCo₂O₄ nanowires have shown better supercapacitor performance than Co₃O₄. However, NiCo₂O₄ nanowires/Ni(OH)₂ core/shell formation and its supercapacitor performance are unclear. It is interesting to find out whether the supercapacitor performance can be increased if the nanowire core is changed to NiCo₂O₄ as the substrate for the growth of the same Ni(OH)₂ shell. It is more interesting to find whether a partial substitution of Co by Ni in the core can significantly affect the growth and performance of Ni(OH)₂ shell. A comparative study on the Ni(OH)₂ shell growing on Co₃O₄ and NiCo₂O₄ nanowire core materials and their performances in supercapacitor devices are worth to be conducted.

In this work, we carried out a comparative study on supercapacitor performances for the core/shell structures of Ni(OH)₂ grown on two different nanowires: NiCo₂O₄ and Co₃O₄. It was found that NiCo₂O₄/Ni(OH)₂ core/shell structure interestingly showed a great improvement in supercapacitor performance comparing with the Co₃O₄/Ni(OH)₂ core/shell electrode. The volumetric and gravimetric capacitances increased 93% and 56%, respectively. And the capacitance retention also enhanced to 96.5% for the NiCo₂O₄/Ni(OH)₂ electrode compared with the Co₃O₄/Ni(OH)₂ (74.4%) after 1000 cycles. Both the enhancement of the specific mass-loading of the Ni(OH)₂ shell and the more electrochemically active NiCo₂O₄ core contributed to its superior performances. Through theoretical simulations, the chemical adsorption energy between the NiCo₂O₄ core and Ni(OH)₂ shell was found to be smaller than that of the Co₃O₄/Ni(OH)₂ structure, which revealed the mechanisms behind the influences of such a compositional change in the nanowire core material on the core/shell's properties. In addition, asymmetric supercapacitor devices were fabricated to demonstrate their great potentials for practical applications. The experimental evidences and scientific understandings achieved in this work are of great values for the design and interpretation of other core/shell systems.

Results and Discussion

The core/shell electrode preparation involves a hydrothermal deposition of Ni-Co-O nanowire cores on nickel foam (NF) and a chemical bath deposition of Ni(OH)₂ shells on the nanowires as illustrated in Fig. S1.

SEM images of the cores, Co₃O₄ and NiCo₂O₄ nanowires, and the core/shell structures, Co₃O₄/Ni(OH)₂ and NiCo₂O₄/Ni(OH)₂, are shown in Fig. 1. Uniform coverages of Co₃O₄ and NiCo₂O₄ nanowires on NFs are observed in Fig. 1a,b. Their insets provide the magnified images of these nanowires. It is clear that the Co₃O₄ and NiCo₂O₄ nanowires are well assembled with 3D network architectures, which are favorable to provide large surface areas for further active material growth. The mass-loadings for the Co₃O₄ and NiCo₂O₄ nanowires are 19.3 mg and 20.9 mg as shown in Table 1(I). After chemical bath deposition of Ni(OH)₂, both the NF/Co₃O₄/Ni(OH)₂ and

(I)						
Electrodes	Loading of core (mg)	Loading of shell (mg)	Loading of core/shell (mg)	SA-C (m ²)	ΔE_a (eV)	
NF/Co ₃ O ₄ /Ni(OH) ₂	19.3	28.3	47.6	2.83	−2.17	
NF/NiCo ₂ O ₄ /Ni(OH) ₂	20.9	37.7	58.6	2.42	−3.10	
(II)						
Electrodes	Specific capacitance of core			Specific capacitance of core/shell		
	G (F/g)	V (F/cm ³)	A (F/cm ²)	G (F/g)	V (F/cm ³)	A (F/cm ²)
NF/Co ₃ O ₄ /Ni(OH) ₂	865	21.0	4.2	1330	79.1	15.8
NF/NiCo ₂ O ₄ /Ni(OH) ₂	1241	32.5	6.5	2079	152.5	30.5

Table 1. (I): The values of loading of core, loading of shell, loading of core/shell, surface area of NF/core (SA-C), and simulated adsorption energy between core and shell (ΔE_a) for the NF/Co₃O₄/Ni(OH)₂ and NF/NiCo₂O₄/Ni(OH)₂ electrodes. (II): Specific capacitance of core and specific capacitance of core/shell at a current density of 2.5 mA/cm² are listed for the NF/Co₃O₄/Ni(OH)₂ and NF/NiCo₂O₄/Ni(OH)₂ electrodes, respectively. The gravimetric (G), volumetric (V) and areal (A) specific capacitance values are all presented.

Figure 2. XRD patterns of (a) NF/Co₃O₄ and NF/Co₃O₄/Ni(OH)₂, and (b) NF/NiCo₂O₄ and NF/NiCo₂O₄/Ni(OH)₂ samples.

NF/NiCo₂O₄/Ni(OH)₂ electrodes turn to be light green as shown in the insets of Fig. 1a',b'. Figure 1a',b' and their insets demonstrate a good coverage and uniform growth of nanostructured gauze-like Ni(OH)₂ shells wrapping the Co₃O₄ and NiCo₂O₄ nanowire cores, but a more complete coverage appears at the sample with NiCo₂O₄ nanowire cores. And the mass-loadings of Ni(OH)₂ shell on the Co₃O₄ and NiCo₂O₄ nanowires are 28.3 mg and 37.7 mg as seen in Table 1(I).

XRD patterns of the NF/Co₃O₄ and NF/Co₃O₄/Ni(OH)₂ samples and the NF/NiCo₂O₄ and NF/NiCo₂O₄/Ni(OH)₂ samples are presented in Fig. 2a,b, respectively. The peaks at 44.4°, 51.6° and 76.1° in all of these samples are assigned to (111), (200) and (220) planes of the metallic Ni phase (JCPDS #01-1258). In Fig. 2a, the peaks at 31.3°, 36.9° and 44.8° are indexed to (220), (311) and (440) planes of the Co₃O₄ phase (JCPDS #42-1467). The peaks at 31.1°, 36.7° and 44.6° can be indexed to (220), (311) and (440) planes of NiCo₂O₄ (JCPDS #20-0781) in Fig. 2b. In the XRD patterns of the NF/Co₃O₄/Ni(OH)₂ and NF/NiCo₂O₄/Ni(OH)₂ electrodes, in addition to the peaks referring to the NF/Co₃O₄ and NF/NiCo₂O₄ cores, the diffraction peaks at 23.8°, 33.7° and 59.6° belongs to (002), (110) and (300) planes of α -Ni(OH)₂ phase (JCPDS #22-0444).

EDS results for Co₃O₄ and NiCo₂O₄ nanowires are obtained using the transmission electron microscope equipped with EDS facility as shown in Fig. 3. To distinguish Ni and Co, the profiles in the energy region between 6.5 keV and 8 keV are magnified in the inset. For the Co₃O₄ nanowire, only Co K_{α1} (6.931 keV) and Co K_{β1} (7.649 keV) peaks are detected. For the NiCo₂O₄ nanowire, additional Ni K_{α1} (7.480 keV) and Ni K_{β1} (8.267 keV) peaks appear. The EDS spectra data analysis reveals a Ni/Co ratio close to the formulated ratio for NiCo₂O₄, but

Figure 3. EDS profiles of Co_3O_4 and NiCo_2O_4 nanowires, and the signals in the energy range from 6.5 keV to 8.5 keV are magnified in the inset.

Figure 4. STEM and elemental mapping images of (a) Co_3O_4 and (b) NiCo_2O_4 nanowires, and (a') $\text{Co}_3\text{O}_4/\text{Ni}(\text{OH})_2$ and (b') $\text{NiCo}_2\text{O}_4/\text{Ni}(\text{OH})_2$ core/shell structures, respectively.

this ratio cannot be accurate due to the overlapping of $\text{Ni } K_{\alpha 1}$ and $\text{Co } K_{\beta 1}$ peaks. The Cu and C signals come from the TEM grid.

Individual core and core/shell wires are inspected by using scanning transmission electron microscopy (STEM) and elemental mapping. The STEM and elemental mapping images in Fig. 4 show (a) evenly distributed Co and O elements in the Co_3O_4 nanowire core and (b) Ni, Co and O elements in the NiCo_2O_4 core. For $\text{Co}_3\text{O}_4/\text{Ni}(\text{OH})_2$ core/shell (Fig. 4a') and $\text{NiCo}_2\text{O}_4/\text{Ni}(\text{OH})_2$ core/shell (Fig. 4b'), the STEM and elemental mapping images reveal core/shell structures with the nanowire cores surrounded by the $\text{Ni}(\text{OH})_2$ flake shell. It can be found that more $\text{Ni}(\text{OH})_2$ flakes are on the NiCo_2O_4 nanowire, in comparison to the $\text{Ni}(\text{OH})_2$ on the Co_3O_4 nanowire, which is in consistent with the SEM observation. The reasons of more $\text{Ni}(\text{OH})_2$ grown on the NiCo_2O_4 nanowire will be discussed later.

The high resolution TEM images of the Co_3O_4 and NiCo_2O_4 cores (Fig. 5a,b) show clear lattice fringes with spacing values of 0.285 nm for the (220) plane of Co_3O_4 and 0.287 nm for the (220) plane of NiCo_2O_4 , respectively.

Figure 5. High resolution TEM images of (a) Co_3O_4 and (b) NiCo_2O_4 cores, and $\text{Ni}(\text{OH})_2$ shells on (a') Co_3O_4 and (b') NiCo_2O_4 core, respectively.

For the flakes, lattice fringes with spacing values of 0.266 nm and 0.231 nm as indicated in Fig. 5a',b' correspond to the (110) and (200) planes of the α - $\text{Ni}(\text{OH})_2$ phase (JCPDS #22-0444).

Herein, it can be concluded that the core/shell structures consisting of the Co_3O_4 or NiCo_2O_4 nanowire core and the flaky $\text{Ni}(\text{OH})_2$ shell are successfully deposited on the nickel foam substrate. Counted on their favorable nanostructures of large surface areas and good coverages over the substrates with considerable loadings, it is desired to have good electrochemical performances for these core/shell electrodes in supercapacitor devices.

The capacitive performances of the $\text{NF}/\text{Co}_3\text{O}_4$, $\text{NF}/\text{NiCo}_2\text{O}_4$, $\text{NF}/\text{Co}_3\text{O}_4/\text{Ni}(\text{OH})_2$ and $\text{NF}/\text{NiCo}_2\text{O}_4/\text{Ni}(\text{OH})_2$ electrodes were characterized and shown in Fig. 6. CV curves of $\text{NF}/\text{Co}_3\text{O}_4$ and $\text{NF}/\text{NiCo}_2\text{O}_4$ are shown in Fig. 6a. One pair of redox reaction peaks at 0.08 V and 0.26 V for the $\text{NF}/\text{Co}_3\text{O}_4$ electrode suggests cobalt ion states transformation during the potential sweep^{50,51}. Distinct two pairs of redox reactions are observed at 0.14 V, 0.02 V and 0.19 V, 0.09 V in the $\text{NF}/\text{NiCo}_2\text{O}_4$ electrode, which is similar to the reported features of NiCo_2O_4 based electrodes^{52,53}. In addition, the CV curve of a bare NF presents a negligible contribution compared with the nanowire core coated electrodes in Fig. 6a. The enclosed area of the CV loop for $\text{NF}/\text{NiCo}_2\text{O}_4$ is also larger than $\text{NF}/\text{Co}_3\text{O}_4$, indicating a larger capacitance value of $\text{NF}/\text{NiCo}_2\text{O}_4$ than $\text{NF}/\text{Co}_3\text{O}_4$. This is consistent with the longer discharging time in the discharge curve of $\text{NF}/\text{NiCo}_2\text{O}_4$ than $\text{NF}/\text{Co}_3\text{O}_4$ in Fig. 6b. The calculated gravimetric, volumetric and areal specific capacitances of core and core/shell electrodes at a current density of $2.5 \text{ mA}/\text{cm}^2$ are presented in Table 1(II). The current density dependent discharge and specific capacitance curves for those core and core/shell electrodes are also presented in Figs S2 and S3. It should be pointed out that in this work the specific capacitance (SC) values were calculated from the discharge measurements, following Equation (1),

$$SC = \frac{It}{(G/V/A)\Delta V} \quad (1)$$

Figure 6. CV curves of (a) bare NF, NF/Co₃O₄ and NF/NiCo₂O₄ electrodes and (c) NF/Co₃O₄/Ni(OH)₂ and NF/NiCo₂O₄/Ni(OH)₂ electrodes at a scan rate of 1 mV s⁻¹, (b) Galvanostatic discharge curves of NF/Co₃O₄, NF/NiCo₂O₄, NF/Co₃O₄/Ni(OH)₂ and NF/NiCo₂O₄/Ni(OH)₂ electrodes at a discharge current density of 2.5 mA/cm², respectively, (b) Capacitance retention of the NF/Co₃O₄/Ni(OH)₂ and NF/NiCo₂O₄/Ni(OH)₂ electrodes at a charge-discharge current of 50 mA/cm² for 1000 cycles.

where I and t are the discharge current and time and ΔV (V) is the potential window. G , V or A is the mass, volume or area of the electrode, referring to specific gravimetric (G), volumetric (V) or areal (A) capacitance, respectively. The gravimetric values are based on the active materials.

Table 1(II) shows a 43% higher gravimetric capacitance for NF/NiCo₂O₄ than NF/Co₃O₄. The volumetric and areal capacitances for NF/NiCo₂O₄ are 55% higher than those for NF/Co₃O₄. After Ni(OH)₂ loading, the discharge time for both the NF/Co₃O₄/Ni(OH)₂ and NF/NiCo₂O₄/Ni(OH)₂ electrodes are much prolonged comparing with their respective NF/core samples in Fig. 6b, which reveals much increased capacitances attributed to the Ni(OH)₂ shell for both core/shell electrodes. The gravimetric specific capacitance for NF/NiCo₂O₄/Ni(OH)₂ is 2079 F/g, which is 68% higher than that of NF/NiCo₂O₄. The gravimetric specific capacitance for NF/Co₃O₄/Ni(OH)₂ is 1330 F/g, 54% higher than that of NF/Co₃O₄. Furthermore, the longer discharging time of NF/NiCo₂O₄/Ni(OH)₂ than NF/Co₃O₄/Ni(OH)₂ also expresses a higher capacitance of NF/NiCo₂O₄/Ni(OH)₂ when comparing with NF/Co₃O₄/Ni(OH)₂. Moreover, the gravimetric and volumetric specific capacitances of NF/NiCo₂O₄/Ni(OH)₂ contrasting to NF/Co₃O₄/Ni(OH)₂ are increased about 56% and 93%, which are much larger than the relative loading increase of Ni(OH)₂ (36%). Therefore, it can be concluded that the increased loading of Ni(OH)₂ shell results in a crucial capacitance enhancement, but the capacitances of the core/shell electrodes are not fully contributed by the Ni(OH)₂ shell but also counted on the cores' contribution. Additional evidences are provided by the CV curves of the NF/Co₃O₄/Ni(OH)₂ and NF/NiCo₂O₄/Ni(OH)₂ electrodes in Fig. 6c. After the growth of Ni(OH)₂ shell, the enclosed areas of CV loops for both core/shell electrodes are significantly extended in contrast to their core electrodes (Fig. 6a). Similar phenomena were also observed in other Ni/Co oxides or hydroxides based core/shell electrodes^{12,39,53–55}. Comparing with NF/Co₃O₄/Ni(OH)₂, there are traceable characteristics of left-shifted electrochemical reaction peaks in NF/NiCo₂O₄/Ni(OH)₂, which could be resulted from the similar features in the CV loops of their cores in Fig. 6a. In Fig. 6d, the cycling performances of these two core/shell electrodes are examined at a charge-discharge current of 50 mA/cm². After 1000 cycles, the residual capacitance of NF/NiCo₂O₄/Ni(OH)₂ is 96.5%, which is much higher than that of NF/Co₃O₄/Ni(OH)₂ (74.4%).

It is found that the NF/NiCo₂O₄/Ni(OH)₂ has much better capacitive performances than NF/Co₃O₄/Ni(OH)₂. The more electrochemically active nature of the NiCo₂O₄ nanowire than Co₃O₄ plays a role, however the much enhanced mass-loading of Ni(OH)₂ shell on the NiCo₂O₄ core than Co₃O₄ contribute more to their capacitances. In order to find out the reasons for the loading increase of the Ni(OH)₂ shells on the NiCo₂O₄ core, the microstructures of the cores, especially the surface area, need to be examined, because the cores instead of bare nickel foams now serve as the effective substrates for the Ni(OH)₂ growth.

Figure 7. (a) Nitrogen adsorption-desorption isotherms with TEM images in the insets and (b) pore size distribution curves of the Co₃O₄ and NiCo₂O₄ nanowire cores.

The analysis of the surfaces and pores of the Co₃O₄ and NiCo₂O₄ cores is performed through N₂ adsorption-desorption isotherm together with TEM images as shown in Fig. 7. The mesoporous nature of the nanowire cores are revealed by a type-IV adsorption-desorption isotherm for both Co₃O₄ and NiCo₂O₄ in Fig. 7a⁵⁶. The hysteresis loop for the Co₃O₄ can be further classified to type H3, which indicates slit-like pores. The hysteresis loop for the NiCo₂O₄ belongs to type H4, indicating slit-like pores with larger pore sizes⁵⁷. In addition, the hysteresis loop of the Co₃O₄ core initiates at a larger relative pressure than NiCo₂O₄, suggesting a relative smaller pore size in the Co₃O₄ core⁵⁷. In Fig. 7b, the Barret-Joyner-Halenda (BJH) pore size distribution curves give a pore size of 7.3 nm for the Co₃O₄ and 17.2 nm for the NiCo₂O₄. In the TEM images in Fig. 7a, narrow slit-like pores are formed as the gaps between the Co₃O₄ or NiCo₂O₄ grains, and the size of pores in the NiCo₂O₄ is relatively larger than that in the Co₃O₄. Besides, the larger area enclosed by the hysteresis loop of the Co₃O₄ nanowire than that of the NiCo₂O₄ nanowire indicates its bigger pore volume and the Brunauer-Emmet-Teller (BET) surface areas of the Co₃O₄ and NiCo₂O₄ cores are 146.6 and 115.8 m² g⁻¹, respectively.

Table 1(I) reveals that the total surface areas of the NF/Co₃O₄ and NF/NiCo₂O₄ electrodes (2 cm × 2 cm) are 2.83 m² and 2.42 m², respectively. When considering the mass-loadings of their Ni(OH)₂ shells, it yields a specific Ni(OH)₂ loading value of 15.8 mg/m² for the NiCo₂O₄, which is 61% higher than that for the Co₃O₄ (9.7 mg/m²). This significant enhancement of the loading capability of Ni(OH)₂ on the NiCo₂O₄ in contrast to Co₃O₄ implies a notable change in the growth rate of Ni(OH)₂ on Co₃O₄ by replacing 1/3 cobalt with nickel at the same deposition duration.

Generally, growth rate (*r*) follows a kinetic law written as⁵⁸,

$$r \propto C e^{-\frac{\Delta E_a}{RT}} \quad (2)$$

where *R* and *C* are constants, and ΔE_a is the chemical affinity, *i.e.* the system energy change before and after growth. In this case, ΔE_a is defined as the adsorption energy and expressed as:

$$\Delta E_a = E_{ad} - (E_c + E_r) \quad (3)$$

Here, E_{ad} is the total energy per cluster of Ni(OH)₂ unit on respective nanowire core system, E_c is the total energy of clean systems and E_r is the total energy of per cluster of Ni(OH)₂.

Figure 8. Molecular models of Ni(OH)_2 on (a) Co_3O_4 and (b) NiCo_2O_4 for adsorption energy simulation.

To reveal this variation of chemical affinity between the cores and Ni(OH)_2 shell, the adsorption energy of Ni(OH)_2 unit on the core surfaces are calculated using density functional theory (DFT) with the generalized gradient approximation of Perdew and Zunger and Ion cores modeled with projector augmented wave (PAW) potentials as implemented in the VASP^{59–61}. All calculations were performed with an energy cutoff of 500 eV, which has been tested for total energy convergence. For unit-cell calculations, a dense Monkhost-Pack grid of $8 \times 8 \times 8$ k-points sampling was used and reduced to $2 \times 2 \times 1$ k-points samples on nanowire or surface calculations. The convergence for energy was chosen as 10^{-5} eV between two ionic steps, and the maximum force allowed on each atom is $0.02 \text{ eV}\text{\AA}^{-1}$. The cluster of Ni(OH)_2 sourced from Ni(OH)_2 crystal with a Trigonal *P*-3*M*1 structure was put in a cubic box with the lattice constant of 15 Å, the relative ground state energy was used to as reference state energy. Here, Co_3O_4 nanowire is considered as the prototype, which has 36 Co and 48 O atoms in its primitive unit cell. The ideal nanowire is cut initially from optimized bulk Co_3O_4 crystal and, subsequently, all atoms are fully optimized. Upon relaxation, the structure of ideal clean Co_3O_4 nanowire reconstructed and which was adopted for adsorption calculations shown in Fig. 8a. Using Ni to replace tetrahedron Co in Co_3O_4 nanowire forms NiCo_2O_4 nanowire containing 24 Co, 12 Ni and 48 O atoms as shown in Fig. 8b.

After simulation, theoretical adsorption energy (ΔE_a) values of -3.10 eV for Ni(OH)_2 on NiCo_2O_4 and -2.17 eV for Co_3O_4 are calculated. The negative values reveal decreased total energies for both cases after deposition. But the lower ΔE_a of the $\text{NiCo}_2\text{O}_4/\text{Ni(OH)}_2$ core/shell indicates a more favorable growth of Ni(OH)_2 on the NiCo_2O_4 than Co_3O_4 , which is well supported by the experimental observation of a much higher mass-loading of Ni(OH)_2 on the NiCo_2O_4 than Co_3O_4 (see Table 1(I)). As a result, the capacitive performances of the core/shell electrodes are going to be affected by their respective cores and subsequent Ni(OH)_2 shells. Additionally, the active material's parting from electrodes during cycling is one of the major concerns for the capacitance loss in literature. In our case, the calculated smaller adsorption energy between Ni(OH)_2 and NiCo_2O_4 than Co_3O_4 also indicates a stronger connection between Ni(OH)_2 and NiCo_2O_4 , which is responsible to its better cycling ability as shown in Fig. 6d.

The NF/ $\text{NiCo}_2\text{O}_4/\text{Ni(OH)}_2$ electrode is applied as the anode in an asymmetric supercapacitor cell that is assembled with a NF/reduced graphene oxide (RGO) as the cathode and a 6 M KOH aqueous solution as the electrolyte (see the inset of Fig. 9a). A practical application case of this supercapacitor cell as the power supply for a mini fan is manifested in Fig. 9a.

The CV curves in Fig. 9b show great electrochemical activities of the both cell over a large potential range from 0 to 1.7 V in the aqueous electrolyte at a scan rate of 5 mV/s. But the cell consisting of NF/ $\text{NiCo}_2\text{O}_4/\text{Ni(OH)}_2$ electrode presents an extra pair of peaks around 0.6 V and 13.5 V, which could be attributed to the more active NiCo_2O_4 nanowire core as revealed in the half cell test (Fig. 6). Galvanostatic discharge curves shown in Fig. 9c give rise to areal specific capacitance values of 6.5 Fcm^{-2} and 7.5 Fcm^{-2} at a discharge current density of 2.5 mAcm^{-2} , respectively. Additional current density dependent discharge curves are presented in Fig. S4. In the Ragone plot in Fig. 9d, the maximum energy density of the NiCo_2O_4 nanowire based cell is found over 44.5 Whkg^{-1} at a power density of 86.3 Wkg^{-1} . Even at a high power density of 3095.3 Wkg^{-1} , its energy density can reach a value of 25.5 Whkg^{-1} . The Ragone plot of the Co_3O_4 based cell reveals an energy density 41.9 Whkg^{-1} at a power density of 36.1 Wkg^{-1} and at a relatively high power density of 1661.1 Wkg^{-1} , its energy density is decreased to 18.4 Whkg^{-1} . Hence, comparing with the Co_3O_4 nanowire based cell, the NiCo_2O_4 nanowire based one has overwhelming advantages in device performances and application potentials.

Figure 9. (a) Photograph of a working mini fan powered by the supercapacitor cell with an inset showing schematic illustration of the device structure (b) CV curves, (c) Galvanostatic discharge curves at a current density of 2.5 mA/cm² and (d) Ragone plots for the asymmetric supercapacitors consisting of NiCo₂O₄/Ni(OH)₂ and Co₃O₄/Ni(OH)₂ core/shell structures and RGOs as two electrodes, respectively.

Conclusions

Co₃O₄/Ni(OH)₂ and NiCo₂O₄/Ni(OH)₂ core/shell structures were successfully prepared on nickel foam substrate through hydrothermal and chemical bath depositions. These core/shell electrodes were applied in a full asymmetry supercapacitor device with reduced graphene oxide as the cathode and KOH aqueous solution as the electrolyte. The great application potentials were demonstrated by the practical case and capacitive characterizations. More interestingly, comparative studies of the NiCo₂O₄/Ni(OH)₂ and Co₃O₄/Ni(OH)₂ core/shell electrodes revealed their distinct capacitive behaviors and different loading ability of Ni(OH)₂ shell. And the causes were further investigated through theoretical simulation and surface analysis of the core/shell interfaces. It was found that the adsorption energy of Ni(OH)₂ on NiCo₂O₄ is smaller than Co₃O₄, which resulted in more Ni(OH)₂ shell loading and better cycling stability of NiCo₂O₄/Ni(OH)₂ electrode. In this work, in addition to an exploration of the NiCo₂O₄ nanowire/Ni(OH)₂ core/shell based electrode for supercapacitor applications, a comprehensive understanding of the core materials and their impacts on the core/shell structures and finally the performances of the whole cell was established. It is of great practical values to analyze various core/shell structures and develop better electrode candidates for supercapacitors.

Methods

Nanowires synthesis. The spinel NiCo₂O₄ nanowires were synthesized by a facile hydrothermal method. 5 mmol of a mixture of NiSO₄·6H₂O and CoSO₄·7H₂O (Ni:Co = 1:2), 10 mmol of NH₄F and 25 mmol of urea were dissolved in 25 mL of de-ionized water under constant stirring. Commercially available analytical graded precursor chemicals were used without further purification. After 10 minutes of stirring, a transparent homogeneous solution was obtained and transferred into Teflon-lined stainless steel autoclaves. Clean nickel foams (2 cm × 2 cm) were subsequently immersed into the above aqueous solution. The sealed autoclave was then heated at 120 °C for 5 hours, and then naturally cooled down to room temperature. The NiCo₂O₄ nanowire coated nickel foam was ultrasonicated in de-ionized water for 1 minute, followed by drying at 120 °C and calcination at 250 °C in air. The Co₃O₄ nanowires were synthesized and treated similarly, except that no Ni precursor was used.

Core/Shell nanowires synthesis. To grow Ni(OH)₂ shell, a precursor was prepared by mixing 40 mL of 1 M NiSO₄·6H₂O, 30 mL of 0.25 M K₂S₂O₈, 10 mL of aqueous ammonia (24% NH₃·H₂O) and 20 mL of de-ionized water in a 250 mL Pyrex beaker at room temperature. The NiCo₂O₄ or Co₃O₄ nanowire coated Ni foam (NF/NiCo₂O₄ or NF/Co₃O₄) was immersed into the precursor. After 15 minutes, the Ni(OH)₂ coated NF/NiCo₂O₄ or

NF/Co₃O₄, i.e. NF/NiCo₂O₄/Ni(OH)₂ or NF/Co₃O₄/Ni(OH)₂ electrode was subjected to a high speed rotation rinsing at 500 rpm for 3 minutes and then dried at 120 °C in air.

Cathode electrode fabrication. A mixture paste of 90 wt% reduced graphene oxide (Graphene Supermarket) and 10 wt% PTFE was spread onto a 2 cm × 2 cm Ni foam to form the RGO-based cathode. Then the electrode was dried at 70 °C in air for 2 hours, pressed at 8 MPa, and then kept at 120 °C in air for 12 hours.

Assembly of the asymmetric supercapacitor. An asymmetric supercapacitor was fabricated with an integrated NF/NiCo₂O₄/Ni(OH)₂ or NF/Co₃O₄/Ni(OH)₂ anode, an RGO/NF cathode and 6 M KOH electrolyte.

Material and device characterizations. The morphology and microstructure of the synthesized core/shell electrodes were characterized by scanning electron microscopy (SEM, Zeiss) and transmission electron microscopy (TEM, JEOL 2010) with energy dispersive X-ray (EDS) analyzer. The structure was measured by X-ray diffraction (XRD) (BRUKER D8 ADVANCE), selected area electron diffraction (SAED) and high resolution TEM. The surface area and porosity of nanowire cores were evaluated by Brunauer–Emmett–Teller (BET, Micromeritics ASAP 2020) N₂ adsorption–desorption measurements. Electrochemical measurements of single electrodes in a half cell were carried out in a three-electrode arrangement with the prepared electrode as working electrode, a platinum plate as counter electrode and a saturated calomel electrode (SCE) as reference electrode in 6 M KOH aqueous electrolyte. Cyclic voltammetry (CV) and galvanostatic charge/discharge test of respective single electrodes and full cells were evaluated by Solartron Electrochemical System SI 1287.

References

- Wang, G., Zhang, L. & Zhang, J. A review of electrode materials for electrochemical supercapacitors. *Chem. Soc. Rev.* **41**, 797–828 (2012).
- Miller, J. R. & Simon, P. Electrochemical capacitors for energy management. *Science* **321**, 651–652 (2008).
- Kötz, R. & Carlen, M. Principles and applications of electrochemical capacitors. *Electrochim. Acta* **45**, 2483–2498 (2000).
- Simon, P. & Gogotsi, Y. Materials for electrochemical capacitors. *Nat. Mater.* **7**, 845–854 (2008).
- Conway, B. E. Transition from “supercapacitor” to “battery” behavior in electrochemical energy storage. *J. Electrochem. Soc.* **138**, 1539–1548 (1991).
- Yu, A., Chabot, V. & Zhang, J. *Electrochemical supercapacitors for energy storage and delivery: fundamentals and applications*. (CRC Press, Taylor & Francis Group, London 2013).
- Conway, B. E. *Electrochemical Supercapacitor: Scientific Fundamentals and Technological Applications*. (Kluwer Academic/Plenum, New York, 1999).
- Zhang, L. L. & Zhao, X. Carbon-based materials as supercapacitor electrodes. *Chem. Soc. Rev.* **38**, 2520–2531 (2009).
- Béguin, F. & Frackowiak, E. *Carbons for electrochemical energy storage and conversion systems*. (CRC Press, Taylor & Francis Group, London, 2009).
- Zhang, Y. *et al.* Progress of electrochemical capacitor electrode materials: A review. *Int. J. Hydrogen Energy* **34**, 4889–4899 (2009).
- Bose, S. *et al.* Carbon-based nanostructured materials and their composites as supercapacitor electrodes. *J. Mater. Chem.* **22**, 767–784 (2012).
- Jiang, J. *et al.* Recent advances in metal oxide-based electrode architecture design for electrochemical energy storage. *Adv. Mater.* **24**, 5166–5180 (2012).
- Lokhande, C., Dubal, D. & Joo, O.-S. Metal oxide thin film based supercapacitors. *Curr. Appl. Phys.* **11**, 255–270 (2011).
- Qu, Q. *et al.* Electrochemical performance of MnO₂ nanorods in neutral aqueous electrolytes as a cathode for asymmetric supercapacitors. *J. Phys. Chem. C* **113**, 14020–14027 (2009).
- Hu, C.-C., Chang, K.-H., Lin, M.-C. & Wu, Y.-T. Design and tailoring of the nanotubular arrayed architecture of hydrous RuO₂ for next generation supercapacitors. *Nano Lett.* **6**, 2690–2695 (2006).
- Rakhi, R., Chen, W., Cha, D. & Alshareef, H. Substrate dependent self-organization of mesoporous cobalt oxide nanowires with remarkable pseudocapacitance. *Nano Lett.* **12**, 2559–2567 (2012).
- Zhao, T., Jiang, H. & Ma, J. Surfactant-assisted electrochemical deposition of α-cobalt hydroxide for supercapacitors. *J. Power Sources* **196**, 860–864 (2011).
- Salunkhe, R. R., Jang, K., Lee, S.-w. & Ahn, H. Aligned nickel-cobalt hydroxide nanorod arrays for electrochemical pseudocapacitor applications. *RSC Adv.* **2**, 3190–3193 (2012).
- Prasad, K. R. & Miura, N. Electrochemically deposited nanowhiskers of nickel oxide as a high-power pseudocapacitive electrode. *Appl. Phys. Lett.* **85**, 4199–4201 (2004).
- Li, H. *et al.* Amorphous nickel hydroxide nanospheres with ultrahigh capacitance and energy density as electrochemical pseudocapacitor materials. *Nat. Commun.* **4**, 1894 (2013).
- Ni, J., Zhao, Y., Li, L. & Mai, L. Ultrathin MoO₃ nanosheets for superior lithium storage. *Nano Energy* **11**, 129–135 (2015).
- Xia, H., Meng, Y. S., Li, X., Yuan, G. & Cui, C. Porous manganese oxide generated from lithiation/delithiation with improved electrochemical oxidation for supercapacitors. *J. Mater. Chem.* **21**, 15521–15526 (2011).
- Xia, H. *et al.* Hierarchical heterostructures of Ag nanoparticles decorated MnO₂ nanowires as promising electrodes for supercapacitors. *J. Mater. Chem. A* **3**, 1216–1221 (2015).
- Wu, M.-S. & Huang, K.-C. Fabrication of nickel hydroxide electrodes with open-ended hexagonal nanotube arrays for high capacitance supercapacitors. *Chem. Commun.* **47**, 12122–12124 (2011).
- Yan, J. *et al.* Advanced asymmetric supercapacitors based on Ni(OH)₂/graphene and porous graphene electrodes with high energy density. *Adv. Funct. Mater.* **22**, 2632–2641 (2012).
- Gogotsi, Y. & Simon, P. True performance metrics in electrochemical energy storage. *Science* **334**, 917–918 (2011).
- Yang, G.-W., Xu, C.-L. & Li, H.-L. Electrodeposited nickel hydroxide on nickel foam with ultrahigh capacitance. *Chem. Commun.* 6537–6539; doi: 10.1039/B815647F (2008).
- Tao, Y. *et al.* Towards ultrahigh volumetric capacitance: graphene derived highly dense but porous carbons for supercapacitors. *Sci. Rep.* **3**, 2975 (2013).
- Alhebshi, N. A., Rakhi, R. B. & Alshareef, H. N. Conformal coating of Ni(OH)₂ nanoflakes on carbon fibers by chemical bath deposition for efficient supercapacitor electrodes. *J. Mater. Chem. A* **1**, 14897 (2013).
- Tang, Z., Tang, C. h. & Gong, H. A high energy density asymmetric supercapacitor from nano-architected Ni(OH)₂/Carbon nanotube electrodes. *Adv. Funct. Mater.* **22**, 1272–1278 (2012).

31. Dubal, D. P., Gund, G. S., Lokhande, C. D. & Holze, R. Decoration of spongelike Ni(OH)₂ nanoparticles onto MWCNTs using an easily manipulated chemical protocol for supercapacitors. *ACS Appl. Mater. Interfaces* **5**, 2446–2454 (2013).
32. Wu, Z. *et al.* Electrostatic induced stretch growth of homogeneous β -Ni(OH)₂ on graphene with enhanced high-rate cycling for supercapacitors. *Sci. Rep.* **4**, 3669 (2014).
33. Ni, J. *et al.* Strongly coupled Bi₂S₃@CNT hybrids for robust lithium storage. *Adv. Energy Mater.* **4**, 1400798 (2014).
34. Xia, H. *et al.* Facile synthesis of hematite quantum-dot/functionalized graphene-sheet composites as advanced anode materials for asymmetric supercapacitors. *Adv. Funct. Mater.* **25**, 627–635 (2015).
35. Yi, H., Chen, X., Wang, H. & Wang, X. Hierarchical TiN@Ni(OH)₂ core/shell nanowire arrays for supercapacitor application. *Electrochim. Acta* **116**, 372–378 (2014).
36. Zhang, L. *et al.* Enhanced energy storage of a UV-irradiated three-dimensional nanostructured TiO₂-Ni(OH)₂ composite film and its electrochemical discharge in the dark. *J. Electroanal. Chem.* **683**, 55–61 (2012).
37. Tian, W. *et al.* Ni(OH)₂ nanosheet@Fe₂O₃ nanowire hybrid composite arrays for high-performance supercapacitor electrodes. *Nano Energy* **2**, 754–763 (2013).
38. Zhou, W. *et al.* One-step synthesis of Ni₃S₂ nanorod@Ni(OH)₂ nanosheet core-shell nanostructures on a three-dimensional graphene network for high-performance supercapacitors. *Energy Environ. Sci.* **6**, 2216–2221 (2013).
39. Zhu, J. *et al.* Hydrogenated CoO_x nanowire@Ni(OH)₂ nanosheet core-shell nanostructures for high-performance asymmetric supercapacitors. *Nanoscale* **6**, 6772–6781 (2014).
40. Huang, L. *et al.* Hybrid composite Ni(OH)₂@NiCo₂O₄ grown on carbon fiber paper for high-performance supercapacitors. *ACS Appl. Mater. Interfaces* **5**, 11159–11162 (2013).
41. Tang, C.-H., Yin, X. & Gong, H. Superior performance asymmetric supercapacitors based on a directly grown commercial mass 3D Co₃O₄@Ni(OH)₂ core-shell electrode. *ACS Appl. Mater. Interfaces* **5**, 10574–10582 (2013).
42. Cai, D. *et al.* Three-dimensional Co₃O₄@NiMoO₄ core/shell nanowire arrays on Ni foam for electrochemical energy storage. *ACS Appl. Mater. Interfaces* **6**, 5050–5055 (2014).
43. Han, L., Tang, P. & Zhang, L. Hierarchical Co₃O₄@PPy/MnO₂ core-shell-shell nanowire arrays for enhanced electrochemical energy storage. *Nano Energy* **7**, 42–51 (2014).
44. Hong, W. *et al.* Controllable synthesis of CoAl LDH@Ni(OH)₂ nanosheet arrays as binder-free electrode for supercapacitor applications. *J. Alloy. Compound.* **608**, 297–303 (2014).
45. Huang, L. *et al.* Nickel-cobalt hydroxide nanosheets coated on NiCo₂O₄ nanowires grown on carbon fiber paper for high-performance pseudocapacitors. *Nano Lett.* **13**, 3135–3139 (2013).
46. Liu, J. *et al.* Co₃O₄ Nanowire@MnO₂ ultrathin nanosheet core/shell arrays: a new class of high-performance pseudocapacitive materials. *Adv. Mater.* **23**, 2076–2081 (2011).
47. Liu, X. *et al.* Hierarchical NiCo₂O₄@NiCo₂O₄ core/shell nanoflake arrays as high-performance supercapacitor materials. *ACS Appl. Mater. Interfaces* **5**, 8790–8795 (2013).
48. Lu, Z. *et al.* Hierarchical Co₃O₄@Ni-Co-O supercapacitor electrodes with ultrahigh specific capacitance per area. *Nano Res.* **5**, 369–378 (2012).
49. Ning, F. *et al.* Co₃O₄@layered double hydroxide core/shell hierarchical nanowire arrays for enhanced supercapacitance performance. *Nano Energy* **7**, 134–142 (2014).
50. Zhang, H. *et al.* Hierarchical Mo-decorated Co₃O₄ nanowire arrays on Ni foam substrates for advanced electrochemical capacitors. *J. Mater. Chem. A* **1**, 8593 (2013).
51. Zhou, C., Zhang, Y., Li, Y. & Liu, J. Construction of high-capacitance 3D CoO@polypyrrole nanowire array electrode for aqueous asymmetric supercapacitor. *Nano Lett.* **13**, 2078–2085 (2013).
52. Yu, L., Zhang, G., Yuan, C. & Lou, X. W. Hierarchical NiCo₂O₄@MnO₂ core-shell heterostructured nanowire arrays on Ni foam as high-performance supercapacitor electrodes. *Chem. Commun.* **49**, 137–139 (2013).
53. Zhang, G. *et al.* Nanoforest of hierarchical Co₃O₄@NiCo₂O₄ nanowire arrays for high-performance supercapacitors. *Nano Energy* **2**, 586–594 (2013).
54. Shao, M. *et al.* Core-shell layered double hydroxide microspheres with tunable interior architecture for supercapacitors. *Chem. Mater.* **24**, 1192–1197 (2012).
55. Xu, K. *et al.* Design and synthesis of 3D interconnected mesoporous NiCo₂O₄@Co_xNi_{1-x}(OH)₂ core-shell nanosheet arrays with large areal capacitance and high rate performance for supercapacitors. *J. Mater. Chem. A* **2**, 10090 (2014).
56. Lowell, S. *Characterization of porous solids and powders: surface area, pore size and density*. (Springer Science & Business Media, Norwell, 2004).
57. Rouquerol, J., Rouquerol, F., Llewellyn, P., Maurin, G. & Sing, K. S. *Adsorption by powders and porous solids: principles, methodology and applications*. (Academic press, Elsevier, Kidlington, 2013).
58. Teng, H. H., Dove, P. M. & De Yoreo, J. J. Kinetics of calcite growth: surface processes and relationships to macroscopic rate laws. *Geochim. Cosmochim. Acta* **64**, 2255–2266 (2000).
59. Kresse, G. & Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B* **59**, 1758 (1999).
60. Kresse, G. & Hafner, J. Ab initio molecular dynamics for open-shell transition metals. *Phys. Rev. B* **48**, 13115 (1993).
61. Kresse, G. & Hafner, J. Ab initio molecular-dynamics simulation of the liquid-metal-amorphous-semiconductor transition in germanium. *Phys. Rev. B* **49**, 14251 (1994).

Acknowledgements

The support of Singapore Ministry of Education Academic Research Fund Tier 2 grant R-284-000-125-112 (with project official number of MOE2013-T2-2-138) is appreciated.

Author Contributions

X.Y. and C.T. contributed equally in the major experiments and paper writing in this work. L.Z. contributed in the asymmetric supercapacitor device preparation. Z.G.Y. contributed in the computer simulation. Prof. H.G. supervised the experiments, data analysis and paper writing. All authors reviewed the manuscript.

Additional Information

Supplementary information accompanies this paper at <http://www.nature.com/srep>

Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Yin, X. *et al.* Chemical insights into the roles of nanowire cores on the growth and supercapacitor performances of Ni-Co-O/Ni(OH)₂ core/shell electrodes. *Sci. Rep.* **6**, 21566; doi: 10.1038/srep21566 (2016).

This work is licensed under a Creative Commons Attribution 4.0 International License. The images or other third party material in this article are included in the article's Creative Commons license, unless indicated otherwise in the credit line; if the material is not included under the Creative Commons license, users will need to obtain permission from the license holder to reproduce the material. To view a copy of this license, visit <http://creativecommons.org/licenses/by/4.0/>