This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

This article can be cited before page numbers have been issued, to do this please use: W. Liu, C. Lu, X. Wang, K. Liang and B. K. Tay, J. Mater. Chem. A, 2014, DOI: 10.1039/C4TA04023F.
In-Situ Fabrication Three-Dimensional Ultrathin Graphite/Carbon Nanotubes/NiO Composite as Binder-Free Electrode for High-performance Energy Storage

Wenwen Liu a, ¶, Congxiang Lu a, b, ¶, Xingli Wang a, Kun Liang a, Beng Kang Tay a, b, *
a. Novitas, Nanoelectronics center of excellence, School of Electrical and Electronic Engineering, Nanyang Technological University, Singapore 639798

b. CINTRA CNRS/NTU/THALES, Nanyang Technological University, Singapore 637553

¶ These two authors contribute equally to this work.

* Corresponding author. Tel: +65 67906783. E-mail address: ebktay@ntu.edu.sg.

ABSTRACT Metal oxide materials have attracted considerable attention as promising electrode materials for energy storage, but the use of metal oxides for electrodes still faces some challenges such as attaining high capacity, good cycle stability, and high-rate performance. Therefore, it is urgent and necessary to rationally design electrode architectures and assemble the metal oxides into the desired structures to further enhance their electrochemical performances. Here, a novel 3D electrode architectures consisting of 3D ultra-thin graphite film (UGF)/CNTs uniformly covered by NiO nanosheets are successfully constructed by a chemical vapor deposition and subsequent electrodeposition, which is directly used as bind-free electrodes for supercapacitors and Li-ion batteries, respectively. In such composite structure, 3D UGF/CNTs provide as the substrates for the NiO nanosheets decoration, and act as spacer to stabilize the composite structure, making the active surfaces of NiO nanosheets accessible for electrolyte penetration and accommodating the volume changes during charge/discharge processes.
As expected, 3D UGF/CNTs/NiO as electrode material for supercapacitor shows high specific capacitance (750.8 F·g$^{-1}$ at the current density of 1 A·g$^{-1}$), superior rate performance (capacitance of 575.6 F·g$^{-1}$ at 10 A·g$^{-1}$) and excellent cycle stability (no decay after 3000 cycles). Moreover, the 3D CNTs/UGF/NiO composite also exhibit the enhanced lithium storage properties as anode material for Li-ion batteries.

**KEYWORDS** 3D ultra-thin graphite film/CNTs structure, NiO nanosheets, Supercapacitors, Lithium-ion batteries, Energy storage

1. **Introduction**

   In response to the rapid depletion of fossil fuels and the deterioration of the environmental pollution, energy storage and conversion from alternative clean energy sources have been one of the major challenges. [1-4] Recently, rapidly increasing demands for energy storage of consumer electronic devices and electric vehicles have also called for novel high performance energy storage devices. [5, 6] Therefore, it is urgent to develop new and highly efficient energy-storage devices to resolve the present energy and environmental problems, and meet the higher demands of future systems. [7-12] Among the highly promising candidates, supercapacitors and Li ion batteries (LIBs) have attracted much attention due to their excellent performances, and have also become an essential theme in recent scientific studies and research.

   As the performances of the energy storage devices depend intimately on the properties of their electrode materials, [13, 14] electrode materials are becoming increasingly important for new generation energy conversion and storage devices such as
supercapacitors and LIBs. Among various electrode materials, metal oxides (such as NiO, Co₃O₄, SnO₂, Fe₂O₃, Fe₃O₄, MnO₂, and V₂O₅ etc.) have been paid a great deal of attention as promising electrode materials because of high theoretical capacities and rich redox reactions. In particular, NiO has stood out as one of the most promising materials due to many remarkable features such as high theoretical capacities, high chemical/thermal stability, ready availability, environmental friendliness, and low cost. However, the poor electrical conductivity of NiO limits its rate capability for high power performance and leads to the real experimental specific capacitance far low from its theoretical value. It is therefore urgent and necessary to further boost its electrochemical performances by exploiting some desirable strategies to meet the requirement for practical applications in supercapacitors and LIBs.

To date, various strategies have been formulated to prepare NiO-based electrodes with improved electrochemical performances. One effective strategy is to fabricate nanostructured NiO materials by adjusting morphology (nanowires, nanobelts, nanotubes, nanosheets, nanoflakes, nanospheres, nanoflowers, nanocone arrays), specific surface area and pore size distribution. Nanostructured NiO can improve the electrochemical performances by enlarging the contact area between the electrolyte and the electrodes, as well as shorten the diffusion distances, but this function is limited especially at high rate discharge and long cycling, probably because of their low electrical conductivity, easy agglomeration and large volume change during charge/discharge process. Another effective strategy is to improve its electrical conductivity by cooperating NiO with some carbon materials (such as graphene, carbon nanotubes and acetylene black), and then enhance the electrochemical performances.
Although the above two strategies can effectively improve the electrochemical performances of NiO, they usually suffer from the drawback that the obtained active materials have to be mixed with some binding additives, and then coated on a current collector to evaluate their electrochemical performances. There is no doubt that the addition of polymer binder will not only increase the “dead volume” in electrode materials but also affect the rate performance and so on.

To transcend the above limitations of nanostructured NiO-based materials, it is indispensable to select a proper approach, a proper structure, and a proper combination of various materials to assemble the active materials into the desired structures. Recently, three dimension (3D) self-supported nano-architecture electrodes have attracted much attention owing to the combination of diversified nanostructures’ merits, including high surface in favor of high capacity, stable structures to the benefit of buffering for the volume change and improving the electric conductivity of electrodes, and lower aggregation and collapse in comparison to nanoparticles.\[43, 44\] Currently, the design and optimization of 3D nanostructures have been a new hot topic for high-performance supercapacitors and LIBs.\[44–47\]

Herein, we disclose a new method to prepare the 3D nickel foam/UGF/CNTs/NiO architecture used as the electrode materials for supercapacitors and LIBs, respectively. Carbon nanotubes (CNTs) and ultra-thin graphite film (UGF) constitute the two most exotic classes of functional carbon materials representing one dimensional (1D) and two-dimensional (2D) nanostructures. Apart from the individual properties and applications, a hybrid structure based on UGF and CNTs can have significant technological advantages. Therefore, it can be expected that novel 3D nickel foam/UGF/CNTs/NiO architecture
electrode would show the promising potential in energy storage devices such as supercapacitors and LIBs. The electrochemical results demonstrate that 3D nickel foam/UGF/CNTs/NiO architecture electrode has superior electrochemical properties including high capacity/capacitance, good cycling stability and excellent rate performance.

2. Experimental

All chemicals were in reagent grade and used without further purification. The synthesis procedure of the novel 3D nickel foam/UGF/CNTs/NiO composite is schematically illustrated in Figure 1.

Fabrication of CNTs on 3D nickel foam/UGF 3D nickel foam/UGF/CNTs was synthesized by a two-step chemical vapor deposition (CVD) method with nickel foam as the substrate and ethanol as the carbon source under an atmospheric pressure. Firstly, nickel foam with a diameter of 12 mm was ultrasonically cleaned in acetone, isopropanol and de-ionized water, respectively. Subsequently, the nickel foam was transferred into a quartz tube and kept at 1000 °C for 5 min to clean the nickel surface under Ar/H\textsubscript{2} atmosphere, and then ethanol vapor was introduced into the quartz tube by bubbling Ar/H\textsubscript{2} through ethanol liquid for 10 min. After cooling down to room temperature, nickel foams/UGF treated by O\textsubscript{2} plasma was emerged into ethanol solution containing 0.1 mol·L\textsuperscript{-1} Ni(NO\textsubscript{3})\textsubscript{2} for 5 min. Finally, CNTs were grown by CVD at 700 °C for 10 min.

Synthesis of 3D nickel foam/UGF/CNTs/NiO composite Prior to electrodeposition, 3D nickel foam/UGF/CNTs was treated by O\textsubscript{2} plasma to change the wettability (Figure
The electrochemical deposition of nickel hydroxide precursor was carried out at –0.9 V in 5 mM Ni(NO$_3$)$_2$·6H$_2$O electrolyte using a Solartron (1287+1260) electrochemical workstation in a standard three-electrode system, where the nickel foam/UGF/CNTs, a platinum plate (2 cm × 2 cm × 0.02 cm) and a saturated calomel electrode (SCE) were used as the working electrode, the counter electrode and the reference electrode, respectively. After electrodeposition for 15 min, the sample was carefully rinsed several times with de-ionized water, and dried at 60 °C in air. Subsequently, the sample was annealed at 300 °C for 2 h with a ramping rate of 1 °C·min$^{-1}$ to transform precursor into NiO. The whole fabrication processes were clearly proved by the color change of nickel foam after the successive grown of UGF, CNTs and NiO (Figure S2), respectively. For a comparison, nickel foam/UGF/CNTs and NiO nanosheets on nickel foam/UGF (nickel foam/UGF/NiO) were also prepared under the same annealing temperature in air.

2.2 Morphology and structural characterization

Field emission scanning electron microscope (FESEM, LEO 1550 GEMINI) and transmission electron microscopy (TEM, Model JEM-2100) were used to characterize the morphology and structure of the samples. To prepare the TEM samples, the as-prepared sample was firstly scraped and sonicated in de-ionized water for 2 min, and then a droplet of the obtained suspension was dropped onto TEM grid, followed by naturally drying at ambient conditions. The crystal structures of the samples were analyzed by powder X-ray diffraction (XRD) using a Bruker D8 Advanced X-ray diffractometer with Cu K$_\alpha$ radiation ($\lambda = 0.15418$ nm), recorded with the 2θ ranging from 15 to 70°. X-ray photoelectron spectroscopy (XPS, Model PHI Quantera SXM) with Al anode was used.
for determining elemental chemical state of sample. Raman spectra were collected with a WITEC CRM200 Raman System (532 nm laser, 2.54 eV, WITec, Germany).

2.3 Electrochemical characterization

Supercapacitor performance measurements The supercapacitive performances of the 3D nickel foam/UGF/CNTs/NiO composite were carried out using a Solartron (1287+1260) electrochemical work station at room temperature in a three-electrode system, whereas a slice of platinum and a standard calomel electrode (SCE) were served as the counter and reference electrodes, respectively. The cyclic voltammetry (CV) tests were measured with the potential window from 0 to 0.45 V (vs. SCE) at different scan rates varying from 10 to 100 mV·s⁻¹. The electrochemical impedance spectroscopy (EIS) plots were tested in the frequency ranging from 100 kHz to 0.05 Hz at open circuit potential with an AC perturbation of 5 mV. Galvanostatic charge/discharge tests were measured with the constant current density ranging from 0.5 to 10 A·g⁻¹. The experiments were performed at room temperature in 6.0 M KOH electrolyte solution. The specific capacitance was calculated from the discharge curve by the formula:

\[ C = \frac{I \Delta t}{m \cdot \Delta V} \]  \hspace{1cm} (1)

The specific energy density and power density were defined respectively by:

\[ E = \frac{C \cdot \Delta V^2}{7.2} \]  \hspace{1cm} (2)

And
\[
P = \frac{E \times 3600}{\Delta t}
\]  \hspace{1cm} (3)

where, \( I \) is the constant discharging current (A·g\(^{-1}\)), \( \Delta t \) is the discharge time (s), \( \Delta V \) is the potential window during the discharge process after internal resistance drop (V), \( m \) is the mass of the electrode material (g), \( C \) is the specific capacitance (F·g\(^{-1}\)), \( E \) is the energy density (Wh·kg\(^{-1}\)) and \( P \) is the power density (W·kg\(^{-1}\)).

**Battery performance measurements** In order to investigate the lithium storage performances of the sample, 3D nickel foam/UGF/CNTs/NiO composite was directly assembled into CR 2032 type half cells without any binders or conductive additives while pure Li metal was used as the counter electrode. The assembly was carried out in a glove box filled with pure Ar (Innovative Technology, Inc.). The electrolyte was LiPF\(_6\) (1.0 M) dissolved in ethylene carbonate and diethyl carbonate (EC/DEC, 1:1 by volume). Charge/discharge capacities were measured by galvanostatic cycling the half cells over the potential range of 0.01–3.0 V (vs. Li/Li\(^+\)) in a battery tester (NEWARE BTS-5 V, Neware Technology Co., Ltd.). The CV test was performed using a Solartron (1287+1260) electrochemical work station.

3. Results and discussions

3.1. Morphological and structural characterization

Scanning electron microscopy (SEM) is shown to illustrate the structural and morphological properties of the as-grown nickel foam/UGF, nickel foam/UGF/CNTs network, and nickel foam/UGF/CNTs/NiO core-shell nanocomposites, respectively.
Figure 2a displays the representative SEM image of UGF on nickel foam with the ripples and wrinkles generated from the different thermal expansion. Using UGF as the catalyst support for CVD growth of CNTs, a dense CNTs mesh grows coaxially and uniformly around the UGF skeleton (Figure 2b). The diameters of CNTs are mainly in the range of 10 to 60 nm (Figure 2c), while the length can reach tens of micrometers. Interestingly, CNTs are distinctly interconnected with each other and are self-assembled into 3D network architecture, which is beneficial for the uniform decoration of active material onto the CNTs. It should be mentioned that the CNTs are still well-adhered to the nickel foam/UGF substrate even after being ultra-sounded at 200 W for 10 min (Figure S3), revealing the robust mechanical adhesion between the CNTs and UGF. Therefore, it may be a reliable binder-free integration of the nickel foam/UGF and the in-situ grown CNTs to serve as a composite current collector. As shown in Figure 2d, the surface of 3D nickel foam/UGF/CNTs network is homogeneously covered by NiO nanosheets, which is further confirmed by the uniform distribution of Ni, O and C components over the entire 3D nickel foam/UGF/CNTs/NiO nanocomposites. The corresponding high imagination images (Figure 2e and f) reveal that each CNT are uniformly anchored and wrapped by thin NiO nanosheets, forming a CNTs/NiO core-shell structure. More importantly, there is still the presence of large void space between neighbor CNTs/NiO core-shell nanorods, which is advantageous for facile access of the electrolyte ions especially at a high charge/discharge rate during electrochemical tests.

Extensive TEM investigation has been carried out to further investigate the microstructural feature of bare UGF, UGF/CNTs and UGF/CNTs/NiO composite. Herein, the TEM images of the above-mentioned three samples are peeled off from nickel foam.
As clearly evidenced by the structure at the edge, the UGF consists of several layers of graphene (Figure 3a), revealing its ultrathin body. Figure 3b are typical TEM images of the UGF/CNTs. It can be clearly observed that the root regions of CNTs directly connect to the UGF, assisting to the form of strong adhesion between the CNTs and UGF. High resolution TEM (HRTEM) image given inset of Figure 3b shows that the CNTs constructed by several tens of carbon layers are the multi-walled CNTs characteristic. TEM images of UGF/CNTs/NiO composite (Figure 3c) exhibit that the CNTs are tightly bonded and totally covered with ultrathin NiO nanosheets (Figure 3c), forming a typical CNTs/NiO core/shell architecture, which agrees well with the SEM images. HRTEM image (Figure 3d) displays the periodic fringes of UGF, CNTs and NiO nanosheets. The inset images in Figure 3d show that the adjacent lattice fringes are 0.20 nm and 0.24 nm corresponding to the (111) and (200) lattice spaces of spinel NiO, respectively. Moreover, the selected-area electron diffraction (SAED) pattern (Figure 3e) exhibits well-defined diffraction rings, indicating the crystalline characteristics of the NiO phase in the UGF/CNTs/NiO composite. These rings can be readily indexed to the (111), (200), (220), and (311) planes of the NiO, highly consistent with the XRD results. Additionally, energy dispersive X-ray spectrometry (EDS) spectrum (Figure 3f) shows only peaks of C, Ni and O except for the Cu signal originating from copper grid, demonstrating the high purity of UGF/CNTs/NiO composite.

XRD and Raman spectroscopy are well-known instrumental in characterizing the structure of samples. As shown in Figure 4a, with the exception of the reflections owing to nickel foam, all peaks are indexed to final UGF/CNTs/NiO composite. The diffraction peak around 26.5° is the characteristic peak of carbon (UGF/CNTs), while the diffraction
peaks at 37.2°, 43.5°, and 62.3° match well with the crystal planes of the (111), (002) and (312) of NiO (JCPDS card No. 04-0835) as reported before. The relative broad diffraction peaks reveal that NiO nanosheets in UGF/CNTs/NiO composite are of relatively low crystallinity. Moreover, no impurity peaks are found in the XRD pattern, indicating that the as-synthesized samples have high phase purity. Figure 4b presents the Raman spectra of bare nickel foam/UGF, nickel foam/UGF/CNTs and nickel foam/UGF/CNTs/NiO composite. For bare nickel foam/UGF, two prominent peaks at 1560 and 2700 cm\(^{-1}\) correspond to the characteristic G and 2D bands of defect-free UGF, respectively. Moreover, the integrated intensity ratio between the G and 2D bands (\(I_G/I_{2D}\)) reveals that the UGF is composed of few layer graphene domains. In comparison with Raman spectrum of bare nickel foam/UGF, Raman spectrum of the 3D nickel foam/UGF/CNTs exhibits typical characteristic D, G and 2D peaks of multiwalled carbon nanotubes. Moreover, Raman spectrum of nickel foam/UGF/CNTs/NiO composite not only presents the characteristic D, G and 2D peaks of UGF and CNTs, but also shows several new peaks around 508 cm\(^{-1}\), which are ascribed to the characteristic modes of crystalline Ni–O lattice vibrations existing in the 3D nickel foam/UGF/CNTs/NiO composite.

To give an in-depth understanding of the crystalline structure of the 3D nickel foam/UGF/CNTs/NiO composite, X-ray photoelectron spectroscopy (XPS) measurements are undertaken to investigate the chemical state of the elements in the as-synthesized products. The survey XPS spectrum (Figure 5a) certifies the presence of Ni, O, and C without other elements in the composite, which is consistent with the above EDX and XRD results. As shown in Figure 5b, the peaks located at 852.2–867.6 eV with
a main peak and two satellite peaks and the peaks located at 870.3–884.8 eV with a main peak and a satellite peak are attributed to the Ni 2p$_{3/2}$ and Ni 2p$_{1/2}$ spin–orbit levels of NiO,\textsuperscript{[55,56]} respectively. Apart from these peaks, additional feature peak appears at 855.7 eV as small shoulder, which is presumably due to the presence of a small quantity of Ni$_2$O$_3$ on the surface.\textsuperscript{[55]} Figure 5c shows the deconvoluted C 1s spectra with different oxygen containing functional groups, including the non-oxygenated C in C=C/C=CR at 284.5 eV, the carbon in C-O/C-O-C at 285.6 eV, and the carbon in C=O/O-C=O at 288.4 eV.\textsuperscript{[42,57]} Furthermore, there are two peaks at 529.4 eV and 530.7 eV for O 1s spectrum (Figure. 5d). According to the previous reports, the binding energy peak at 529.4 eV is ascribed to the typical metal–oxygen bond of Ni–O/C=CRNi,\textsuperscript{[42,57]} and the binding energy peak at 530.7 eV is assigned to Ni-OH/C=O,\textsuperscript{[42,57]} including defective nickel oxide with hydroxyl groups absorbed on its surface. Based on the above-mentioned SEM, TEM, XRD, and Raman results, 3D nickel foam/UGF/CNTs/NiO composite with 1D quasi-aligned CNTs/NiO core/shell structure that tightly connected with nickel foam/UGF backbones have been successfully constructed, which is favorable for developing highly conductive and high performance electrodes.

3.2 Supercapacitors performance

Herein, as-prepared 3D nickel foam/UGF/CNTs/NiO composite is directly used as electrode material without introduction of any polymer binders, and its electrochemical performances are characterized by cyclic voltammetry (CV), galvanostatic charge/discharge measurements, and electrochemical impedance spectroscopy (EIS). Figure 6a shows the representative CV curves of 3D nickel foam/UGF/CNTs/NiO composite with the potential window of 0.0–0.45 V in 6.0 M KOH solution at different
scan rates. The CV curve shows a pair of strong redox peaks at 0.19 V and 0.33 V, indicating the pseudocapacitive behavior of the 3D nickel foam/UGF/CNTs/NiO composite from faradaic redox reactions between NiO and NiOOH in alkaline solution as follows: \[ \text{NiO} + \text{OH}^- \leftrightarrow \text{NiOOH} + \text{e}^- \] (4)

Moreover, along with the increase of scan rates from 10 to 100 mV·s\(^{-1}\), the anodic peaks shift positively while the cathodic peaks shift negatively, which are attributed to the polarization of the electrode at the higher scan rates. \[60,61\] Meanwhile, a linear dependence is established between the peak currents (I\(_{pa}\) (anodic peak current) and I\(_{pc}\) (cathodic peak current)) and square root of scan rates from 10 to 100 mV·s\(^{-1}\) (Figure 6b), revealing that the redox reaction of 3D nickel foam/UGF/CNTs/NiO composite in KOH electrolyte is mainly under the diffusion-controlled step. \[62,63\] In addition, as shown in Figure S4, the 3D nickel foam/UGF/CNTs/NiO composite exhibits the largest area surrounded by CV curve among nickel foam/UGF/CNTs, nickel foam/UGF/NiO composite, and nickel foam/UGF/CNTs/NiO composite, indicating the limited contribution of pure nickel foam/UGF/CNTs to the capacitance of 3D nickel foam/UGF/CNTs/NiO composite and the significantly enhanced capacitance due to the unique 3D structure.

To further examine the supercapacitive performances, a series of charge/discharge measurements are performed on 3D nickel foam/UGF/CNTs/NiO composite electrode at various charge/discharge current densities, as shown in Figure 6c. Unlike the case of electric double layer capacitors with linear charge/discharge characteristics, the
charge/discharge curves of 3D nickel foam/UGF/CNTs/NiO composite electrode exhibit the typical pseudocapacitive behavior, which agrees well with the CV results. On the basis of the discharge curves (Figure 6d), the specific capacitances of 3D nickel foam/UGF/CNTs/NiO composite electrode are 815.5, 750.8, 675.3, 620.7, 595.1, and 575.6 F·g\(^{-1}\) at the current densities of 0.5, 1, 2, 4, 7, 10 A·g\(^{-1}\), respectively. The result is comparable or better than those of the reported NiO-based composite materials, such as hierarchical porous NiO nano/micro superstructures (710 F·g\(^{-1}\) at 1 A·g\(^{-1}\)), \[17\] NiO nanosheet arrays on Ni foam (674.2 F·g\(^{-1}\) at 1 A·g\(^{-1}\)), \[28\] 3D NiO/graphene composite (555 F·g\(^{-1}\) at 1 A·g\(^{-1}\)), \[29\] 3D porous graphene macroassembly/NiO hybrid (646 F·g\(^{-1}\) at 0.5 A·g\(^{-1}\)), \[57\] 3D NiO/ultrathin derived graphene hybrid (425 F·g\(^{-1}\) at 2 A·g\(^{-1}\)). \[61\] Additionally, when the charge/discharge current density is increased 20 folds from 0.5 to 10 A·g\(^{-1}\), about 71% of the original capacitance is still retained, demonstrating good rate performance of 3D nickel foam/UGF/CNTs/NiO composite electrode. As shown in Ragone plot (Figure 6e), the power density increases from 100.6 W·kg\(^{-1}\) to 2007.3 W·kg\(^{-1}\) and the energy density decreases from 18.1 Wh·kg\(^{-1}\) to 12.4 Wh·kg\(^{-1}\), respectively, as the discharge current density increase from 0.5 A·g\(^{-1}\) to 10 A·g\(^{-1}\).

Since long cycling life is another very crucial parameter to evaluate the electrode materials for supercapacitors, the cycle stability of 3D nickel foam/UGF/CNTs/NiO composite is investigated by repeating charge/discharge test at a current density of 5 A·g\(^{-1}\) in 6 M KOH solution (Figure 6f). Notably, the specific capacitance is retained at 660 F·g\(^{-1}\) after 3000 cycles, corresponding to 110% of its original value. The slight increase of capacitance is ascribed to the activation effect of electrochemical cycling, suggested by previous reports of other NiO-based electrode materials. \[49, 63\] The cycling
performance of 3D nickel foam/UGF/CNTs/NiO composite is better than previous reports of NiO-based composites. [17, 28, 29, 57] These encouraging results show that the 3D nickel foam/UGF/CNTs/NiO composite possesses the high specific capacitance and excellent cycling stability, which can be used as electrode material in high-performance supercapacitors.

Such intriguing capacitive performances of 3D nickel foam/UGF/CNTs/NiO composite can be mainly attributed to the superior 3D conducting network constructed by UGF, CNTs, as well as the pseudocapacitive behavior of the active material (NiO nanosheets). First, the 3D nickel foam/UGF/CNTs network can offer a large material/electrolyte contact area, a short diffusion distance for electrolyte ions as well as better electrical contact between NiO and current collector. Second, as an excellent host material, CNTs not only can provide a good electrical conducting path for charge transfer and redox kinetics of the deposited layer (NiO nanosheets), but also act as the uniform nucleation sites for NiO and offer more electrochemical active sites by effectively inhibiting the aggregation of NiO. Moreover, ultrathin NiO nanosheets uniformly deposited on the CNTs network can significantly improve the kinetics and the electrochemical utilization of NiO due to the extraordinarily shortened ion diffusion and transport length (Figure S5).

In addition, the good electrical conductivity of CNTs directly in-situ grown on the UGF with robust adhesion can ensure intimate contacts and effective electron transport between the charge collecting substrates of nickel foam/UGF/CNTs and the NiO nanosheets, and avoid the addition of extra additives and conductive binders.

3.3 Li-Ion Batteries Performance
In addition to the supercapacitive performance, the lithium storage properties of the 3D nickel foam/UGF/CNTs/NiO composite are also evaluated in this work. Figure 7a displays the CV curves for the first three cycles of the 3D nickel foam/UGF/CNTs/NiO composite electrode at a scan rate of 0.1 mV·s\(^{-1}\) in the range of 0.01 and 3.0 V. In the first cathodic scan curve, a shoulder at around 0.89 V and an intensive reduction peak centered at 0.51 V correspond respectively to the initial reduction of NiO to metallic Ni nanoparticles, the formation of amorphous Li\(_2\)O (NiO+2Li\(^+\)+2e\(^-\)→ Ni + Li\(_2\)O), and the formation of a partially reversible solid electrolyte interface (SEI) layer.\(^{[30, 36, 37, 64, 65]}\) However, the cathodic peak at 0.51 V shift to 0.98 V during the subsequent cycles, which may be due to the drastic lithium driven, structural, or textural modify cations.\(^{[30, 37]}\) The two broad peaks located at about 1.34 and 2.24 V in the first anodic scan curve are attributed to the partial decomposition of the polymeric coating on the NiO surface, and the decomposition of Li\(_2\)O and oxidation of metallic nickel to NiO (Ni + Li\(_2\)O → NiO + 2Li\(^+\) + 2e\(^-\)), respectively.\(^{[30, 36, 37, 64]}\) The well-known mechanisms for the above-mentioned processes are the reversible reaction of NiO+2Li+2e\(^-\)↔Ni+Li\(_2\)O and the partial composition/decomposition of the SEI layer.\(^{[30, 36]}\) Moreover, the CV curves are stable and well overlapped after the second cycle, indicating high electrochemical reversibility and good capacity retention for the 3D nickel foam/UGF/CNTs/NiO composite electrode.

As shown in the initial discharge curve (Figure 7b), the voltage rapidly falls from 3.0 to 1.1 V, followed by a long plateau region at about 0.73 V, which is relevant to the reduction of NiO to metallic Ni and the formation of SEI layers. Moreover, the specific plateau between 0.12 and 0.07 V is due to the insertion of lithium ion into UGF/CNTs.\(^{[65]}\)
In the first charge profile, there are three plateaus located at 0.1, 1.6, and 2.2 V, which originate from the extraction of lithium ions from UGF/CNTs, the partial decomposition of the SEI layer, and the formation of NiO from Ni, respectively. These results obtained from the first charge/discharge curve are highly consistent with those of CV. The initial discharge and charge capacities are 1359.4 and 963.3 mAh·g\(^{-1}\), respectively, and the irreversible capacity loss of 29.1% is mainly attributed to the possible irreversible processes such as electrolyte decomposition and inevitable formation of a polymer-like SEI layer. It is worth noting that the initial plateau and slope in the second and subsequent cycles are less obvious than the first cycle, also suggesting an irreversible capacity loss in the first cycle.

High rate performance is another important precondition to apply as anode material in high power LIBs. Therefore, the as-prepared 3D nickel foam/UGF/CNTs/NiO is examined with different current densities and the results are given in Figure 7c. The discharge capacities of the 3D nickel foam/UGF/CNTs/NiO at 100, 200, 500, 800, 1000, 1500, and 2000 mA·g\(^{-1}\) are 1143.1, 1097.3, 998.5, 919.9, 867.5, 786.4, and 716.8 mAh·g\(^{-1}\), respectively, demonstrating an excellent high rate performance. It should be noticed that as long as the current rate reverses back to low current rate (100 mA·g\(^{-1}\)), the cell capacity recovers to the original value, indicating that the 3D nickel foam/UGF/CNTs/NiO composite is tolerant of various charge and discharge currents. As shown in previous studies, the high rate performance highly depends on the rapid ionic and electronic diffusion and transport. In our case, the 3D network structure can provide 3D electron conducting channels within the electrode, and facilitate the penetration and diffusion of electrolyte, leading to fast lithium ion transport. And also,
the thin NiO nanosheets can significantly shorten the diffusion distance between lithium ion and electron. Herein, it should be mentioned that the capacity contributed from the Li$^+$ lithiation/delithiation with pure nickel foam/UGF/CNTs is negligible, which can be clearly proved by its value of specific capacity at different current densities (Figure.S6).

Figure 7d displays the cycling performance of the 3D nickel foam/UGF/CNTs/NiO composite at a current density of 200 mA·g$^{-1}$. Encouragingly, the electrode still maintains a specific capacity of 995.3 mA·h·g$^{-1}$ (100.9% of the initial capacity) at the current density of 200 mA·g$^{-1}$ after 100 cycles, which is larger or comparable to the previously reported values for NiO-based nanomaterials, such as mesoporous NiO achieving a capacity of 680 mA·h·g$^{-1}$ after 50 cycles at 0.1 C, $^{[16]}$ hollow NiO nanotubes with a capacity of 600 mA·h·g$^{-1}$ at 200 mA·g$^{-1}$ after 100 cycles, $^{[33]}$ mesoporous NiO nanosheets networks with a capacity of 1043 mA·h·g$^{-1}$ at 0.2 C after 80 cycles, $^{[37]}$ NiO nanosheets/graphene composite with a capacity of 1000 mA·h·g$^{-1}$ after 50 cycle at 50 mA·g$^{-1}$, $^{[42]}$ NiO on vertically-aligned multiwall carbon nanotube arrays with a capacity of 864 mA·h·g$^{-1}$ at 0.2 C after 50 cycles, $^{[64]}$ NiO–Ni/natural graphite with a capacity of 532 mA·h·g$^{-1}$ at 0.15 C after 100 cycles. $^{[65]}$ Meanwhile, the Coulombic efficiency is close to 100% in the overall battery operation, indicating the excellent cycle stability of 3D nickel foam/UGF/CNTs/NiO composite electrode. In addition, it is interesting to note that the slightly increase and then reduce in specific capacity from 2th cycle to 55th cycle may be due to the reversible growth of a polymeric gel-like layer originating from kinetically activated electrolyte degradation and the interfacial lithium storage, which is common for most anode materials. $^{[30,36]}$
Based on the above electrochemical performances, the excellent lithium storage properties of the 3D nickel foam/UGF/CNTs/NiO composite in terms of remarkable rate capability and stable cycling performance can be attributed to the rationally designed nanostructure and composition. Specifically, the 3D network structure, constructed by CNTs/NiO core/shell nanorods growth on the 3D nickel foam/UGF, enables sufficient electrode/electrolyte contact area for high Li$^+$ ion flux across the interface and reduces Li$^+$ ion diffusion length, which promotes the electrochemical processes. Moreover, the local voids between the CNTs/NiO core/shell nanorods could efficiently accommodate the volume change during repeated charge-discharge cycling, thus leading to improved cycling stability.

4. Conclusion

In summary, we present the rational design and fabrication of an interesting 3D nickel foam/UGF/CNTs/NiO composite by a two-step which includes chemical vapor deposition and subsequent electrodeposition. The as-obtained 3D nickel foam/UGF/CNTs/NiO composite can be used as binder-free electrode for supercapacitors and LIBs, respectively. The merits in the unique architectures, structures and morphologies, bring in advantages such as excellent electrical contact between the active materials and current collect, numerous active reaction sites and facile ion diffusion path provided by the large open spaces between neighbor CNTs/NiO core-shell nanorods, and significantly reinforced mechanical strength, enabling their promising performance in supercapacitors and LIBs. Encouragingly, serving as a free-standing electrode for
supercapacitors, 3D nickel foam/UGF/CNTs/NiO composite exhibits a high capacitance of 750.8 F·g\(^{-1}\) at the current density of 1 A·g\(^{-1}\), outstanding rate performance (capacitance of 575.6 F·g\(^{-1}\) at 10 A·g\(^{-1}\)) and excellent cycling stability. Moreover, the 3D nickel foam/UGF/CNTs/NiO composite as anode material for LIBs shows a reversible capacity of 1143.1 mAh·g\(^{-1}\) at a current density of 100 mA·g\(^{-1}\), retaining 100.9% of the initial discharge capacity after 100 cycles a current density of 200 mA·g\(^{-1}\). In addition, this strategy may be extended to synthesize other transition metal oxides with 3D carbon based nanoarchitectures, which are very promising in high performance supercapacitors, LIBs or catalysts because of their unique structural features.

5. References


24, 5045.


2012, 6, 3214.


Figure captions

**Figure 1** Schematics of the fabrication process of 3D nickel foam/UGF/CNTs/NiO composite: CVD growth of UGF on nickel foam (Step 1), CVD growth of CNTs on nickel foam/UGF (Step 2), and deposition and annealing treatment of nickel foam/UGF/CNTs/Ni(OH)$_2$ precursor (Step 3).

**Figure 2** SEM images of (a) 3D nickel foam/UGF, (b, c) 3D nickel foam/UGF/CNTs network, (e, f, and g) 3D nickel foam/UGF/CNTs/NiO core-shell structure. The inset in (a) shows a high-magnified SEM image of (a). The inset in (b) shows a low-magnified SEM image of (b). The inset in (d) shows the element (Ni, O and C) mapping of the marked area in (d).

**Figure 3** TEM images of (a) UGF and (b) UGF/CNTs, (c, d) UGF/CNTs/NiO composite, The corresponding (e) SAED pattern and (f) EDS spectrum of the UGF/CNTs/NiO composite. The inset in (b) shows a high-magnified TEM image of CNTs. The inset in (d) shows the corresponding high-magnified TEM images of the marked area in (d).

**Figure 4** (a) XRD pattern and (b) Raman spectra of the 3D nickel foam/UGF/CNTs/NiO composite. The inset in (b) shows the corresponding Raman spectrum of the marked region in (b).

**Figure 5** XPS spectra of 3D nickel foam/UGF/CNTs/NiO composite: (a) survey scan, (b) Ni 2p, (c) C 1s, and (d) O 1s.

**Figure 6** Electrochemical characterization of supercapacitive performances of the 3D nickel foam/UGF/CNTs/NiO composite: (a) CV curves at various scan rates ranging from 10 to 100 mV·s$^{-1}$; (b) the corresponding plot of anodic and cathodic peak currents.
vs. square root of scan rates; (c) charge/discharge curves at various current densities; (d) the corresponding capacitance as a function of current density; (e) Ragone plot of the estimated energy density and power density at various charge/discharge current densities; (f) cycling performance at a current density of 5 A·g⁻¹. The inset in (f) is the CV curves of the 1st, 1000th, 2000th and 3000th cycle.

Figure 7 lithium storage properties of the 3D nickel foam/UGF/CNTs/NiO composite: (a) the CV curves for first three cycles measured at a scan rate of 0.1 mV·s⁻¹ between 0.01 V and 3 V; (b) voltage capacity profiles at a current density of 100 mA·g⁻¹; (c) rate capabilities at different current rates; (d) specific capacities and Columbic efficiency versus charge/discharge cycle number at a current density of 200 mA·g⁻¹.
**Figure 1** Schematics of the fabrication process of 3D nickel foam/UGF/CNTs/NiO composite: CVD growth of UGF on nickel foam (Step 1), CVD growth of CNTs on nickel foam/UGF (Step 2), and deposition and annealing treatment of nickel foam/UGF/CNTs/Ni(OH)$_2$ precursor (Step 3).
Figure 2 SEM images of (a) 3D nickel foam/UGF, (b, c) 3D nickel foam/UGF/CNTs network, (e, f, and g) 3D nickel foam/UGF/CNTs/NiO core-shell structure. The inset in (a) shows a high-magnified SEM image of (a). The inset in (b) shows a low-magnified SEM image of (b). The inset in (d) shows the element (Ni, O and C) mapping of the marked area in (d).
Figure 3

**Figure 3** TEM images of (a) UGF and (b) UGF/CNTs, (c, d) UGF/CNTs/NiO composite, The corresponding (e) SAED pattern and (f) EDS spectrum of the UGF/CNTs/NiO composite. The inset in (b) shows a high-magnified TEM image of CNTs. The inset in (d) shows the corresponding high-magnified TEM images of the marked area in (d).
Figure 4 (a) XRD pattern and (b) Raman spectra of the 3D nickel foam/UGF/CNTs/NiO composite. The inset in (b) shows the corresponding Raman spectrum of the marked region in (b).
Figure 5 XPS spectra of 3D nickel foam/UGF/CNTs/NiO composite: (a) survey scan, (b) Ni 2p, (c) C 1s, and (d) O 1s.
Figure 6

Electrochemical characterization of supercapacitive performances of the 3D nickel foam/UGF/CNTs/NiO composite: (a) CV curves at various scan rates ranging from 10 to 100 mV·s⁻¹; (b) the corresponding plot of anodic and cathodic peak currents vs. square root of scan rates; (c) charge/discharge curves at various current densities; (d) the corresponding capacitance as a function of current density; (e) Ragone plot of the estimated energy density and power density at various charge/discharge current densities; (f) cycling performance at a current density of 5 A·g⁻¹. The inset in (f) is the CV curves of the 1st, 1000th, 2000th and 3000th cycle.
Figure 7

Figure 7 lithium storage properties of the 3D nickel foam/UGF/CNTs/NiO composite: (a) the CV curves for first three cycles measured at a scan rate of 0.1 mV·s$^{-1}$ between 0.01 V and 3 V; (b) voltage capacity profiles at a current density of 100 mA·g$^{-1}$; (c) rate capabilities at different current rates; (d) specific capacities and Columbic efficiency versus charge/discharge cycle number at a current density of 200 mA·g$^{-1}$. 
3D ultrathin graphite film/CNTs/NiO composite as the electrode material for energy storage exhibits high specific capacitance/capacity, excellent rate capability and good cycle stability.