In situ fabrication of three-dimensional, ultrathin graphite/carbon nanotube/NiO composite as binder-free electrode for high-performance energy storage†

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Metal oxides have attracted considerable attention as promising electrode materials for energy storage, but the use of metal oxides for electrodes still faces challenges such as attaining high capacity, good cycle stability, and high-rated performance. Therefore, rational design of electrode architectures and assembling metal oxides into desired structures to further enhance electrochemical performance is necessary. Here, novel 3D electrode architectures consisting of 3D ultra-thin graphite film (UGF)/carbon nanotubes (CNTs) uniformly covered by NiO nanosheets are successfully constructed by a chemical vapor deposition and subsequent electrodeposition, which are directly used as bind-free electrodes for supercapacitors and Li-ion batteries. In such composite structures, 3D UGF/CNTs serve as substrates for NiO nanosheet decoration, and act as spacers to stabilize the composite structure, making the active surfaces of NiO nanosheets accessible for electrolyte penetration and accommodating volume changes during charge/discharge processes. As expected, 3D UGF/CNTs/NiO as electrode material for supercapacitors showed high specific capacitance (750.8 F g⁻¹ at 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 exhibited enhanced lithium storage properties as anode materials for Li-ion batteries.

1. Introduction

In response to the rapid depletion of fossil fuels and environmental pollution, energy storage and conversion from alternative clean-energy sources have been 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, development of new and highly efficient energy-storage devices is urgent to resolve or alleviate present energy and environmental problems and meet higher demands of future systems.7–12 Among highly promising candidates, supercapacitors and Li-ion batteries (LIBs) have attracted much attention due to excellent performance, and have also become major targets of research and development.

Given that energy-storage device performance depends intimately on the properties of respective electrode materials,13,14 the latter have become increasingly important for new-generation energy conversion and storage devices such as supercapacitors and LIBs. Among various electrode materials, metal oxides (such as NiO,15–17 Co₃O₄,16,19 SnO₂,20,21 Fe₂O₃,22 Fe₃O₄,23 MnO₂,24,25 and V₂O₅26) have garnered a great deal of attention 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.27–30 However, the poor electrical conductivity of NiO limits its rate capability for high-power performance and leads to real experimental specific capacitance far below its theoretical value. It is therefore urgent and necessary to further boost the electrochemical performance of NiO.

To date, various strategies have emerged to fabricate NiO-based electrodes with improved electrochemical performance. One effective strategy is to fabricate nanostructured NiO materials by adjusting morphology (nanowires, nanobelts, nanotubes, nanosheets, nanoflakes, nanospheres, nanoflowers, nanocone arrays),31–37 specific surface area and pore size distribution.38,39 Nanostructured NiO can improve electrochemical performance by enlarging the contact area between the electrolyte and electrodes, as well as shorten diffusion

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distances, but this function is limited especially at high-rate discharge and long cycling, probably because of low electrical conductivity, easy agglomeration and large volume change during the charge/discharge process. Another effective strategy is to improve electrical conductivity by combining NiO with carbon materials (such as graphene, carbon nanotubes and acetylene black),\(^\text{40-42}\) and then enhance electrochemical performance. Although these two strategies can effectively improve the electrochemical performance of NiO, there are drawbacks: obtained active materials must be mixed with binding additives, and then coated onto a current collector. Adding polymer binder not only increases the “dead volume” in electrode materials, but also affects rate performance.

To transcend the abovementioned limitations of nanostructured NiO-based materials, selecting a proper approach, structure, and combination of materials is paramount. Recently, 3D self-supported nanoarchitecture electrodes have attracted much attention owing to a combination of benefits, including greater surface area in favor of high capacity, stable structures to benefit buffering for volume change and improving the electric conductivity of electrodes, and lower aggregation and collapse in comparison to nanoparticles.\(^\text{43,44}\) Currently, the design and optimization of 3D nanostructures for high-performance supercapacitors and LIBs are hot topics.\(^\text{45-48}\)

Herein, we present a new method to prepare the 3D nickel foam/UGF/CNTs/NiO architecture used as 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 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 electrodes would show 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 Fig. 1.

Fabrication of CNTs on 3D nickel foam/UGF

3D nickel foam/UGF/CNTs were synthesized via a two-step chemical vapor deposition (CVD) method with nickel foam as the substrate and ethanol as the carbon source under atmospheric pressure. First, nickel foam with a diameter of 12 mm was ultrasonically cleaned in acetone, isopropanol and deionized water. Subsequently, the nickel foam was transferred into a quartz tube and kept at 1000 °C for 5 min to clean the nickel surface under an Ar/H\(_2\) atmosphere, and then ethanol vapor was introduced into the quartz tube by bubbling Ar/H\(_2\) through ethanol liquid for 10 min. After cooling down to room temperature, nickel foam/UGF treated by O\(_2\) plasma was merged into ethanol solution containing 0.1 mol L\(^{-1}\) Ni(NO\(_3\))\(_2\) for 5 min. Finally, CNTs were grown via CVD at 700 °C for 10 min.

Synthesis of 3D nickel foam/UGF/CNTs/NiO composite

Prior to electrodeposition, the 3D nickel foam/UGF/CNTs were treated by O\(_2\) plasma to change wettability (Fig. S1 ESI†). The electrochemical deposition of nickel hydroxide precursor was carried out at −0.9 V in 5 mM Ni(NO\(_3\))\(_2\)
\(\cdot\)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 \(\times\) 2 cm \(\times\) 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 deionized 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 the precursor into NiO. The entire fabrication process was clearly proved by the color change of nickel foam after successive growth of UGF, CNTs and NiO (Fig. S2 ESI†). For comparison purposes, 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.

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 first scraped and sonicated in de-ionized water for 2 min, and then a droplet of the obtained suspension was dropped onto a TEM grid, followed by natural 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\(_x\) radiation (\(\lambda = 0.15418\) nm), recorded with the 2\(\theta\) ranging from 15 to 70°. X-ray photoelectron spectroscopy (XPS, Model PHI Quantera SXM) with an Al anode was used for determining the elemental chemical state of the sample. Raman spectra were collected with a WITTEC CRM200 Raman System (532 nm laser, 2.54 eV, WITec, Germany).

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 workstation at room temperature in a three-electrode system, whereas a slice of platinum and a standard calomel electrode (SCE) 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:

\[
C = \frac{I \Delta t}{m \Delta V}
\]  

(1)

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

\[
E = \frac{C \Delta V^2}{7.2}
\]  

(2)

and

\[
P = \frac{E \times 3600}{\Delta t}
\]  

(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 the 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 (W h 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 CR2032-type half cells without any binders or conductive additives, while pure Li metal was used as the counterelectrode. Assembly took place in a glovebox 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 via 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 workstation.

**3. Results and discussions**

**Morphological and structural characterization**

Scanning electron microscopy (SEM) was used 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. Fig. 2a displays the representative SEM image of UGF on nickel foam with the ripples and wrinkles generated from different thermal expansions. Using UGF as the catalyst support for CVD growth of CNTs, a dense CNTs mesh was grown coaxially and uniformly

![Fig. 1 Schematics of fabrication process for 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).](image-url)

![Fig. 2 SEM images of (a) 3D nickel foam/UGF; (b and c) 3D nickel foam/UGF/CNTs network; and (e, f and g) 3D nickel foam/UGF/CNTs/NiO core–shell structure. The inset in (a) shows high-magnification SEM image of (a). The inset in (b) shows a low-magnification SEM image of (b). The inset in (d) shows the element (Ni, O, and C) mapping of marked area in (d).](image-url)
around the UGF skeleton (Fig. 2b). CNT diameters were mainly in the range of 10–60 nm (Fig. 2c), while the length could reach tens of micrometers. Interestingly, the CNTs were distinctly interconnected with each other and 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 were still well-adhered to the nickel foam/UGF substrate even after being ultrasounded at 200 W for 10 min (Fig. S3 ESI†), revealing the robust mechanical adhesion between the CNTs and UGF. Therefore, the material may be a reliable binder-free integrator for the nickel foam/UGF and in situ-grown CNTs to serve as a composite current collector. As shown in Fig. 2d, the surface of the 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 all 3D nickel foam/UGF/CNTs/NiO nanocomposites. The corresponding high-magnification images (Fig. 2e and f) reveal that each CNT is uniformly anchored and wrapped by thin NiO nanosheets, forming a CNTs/NiO core–shell structure. More importantly, a large void space between neighboring CNTs/NiO core–shell nanorods remained, which is advantageous for facile access of electrolyte ions, especially at a high charge–discharge rate during electrochemical tests.

Extensive TEM analysis was 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 (Fig. 3a), revealing its ultrathin body. Fig. 3b shows typical TEM images of the UGF/CNTs. It can be clearly observed that the root regions of CNTs directly connect to the UGF, assisting in the formation of strong adhesion between the CNTs and UGF. The high-resolution TEM (HRTEM) image inset in Fig. 3b shows that the CNTs constructed by several tens of carbon layers are characteristically multiwalled CNTs. TEM images of the UGF/CNTs/NiO composite (Fig. 3c) exhibit that the CNTs are tightly bonded and totally covered with ultrathin NiO nanosheets (Fig. 3c), forming a typical CNTs/NiO core–shell architecture, which agrees well with the SEM images. The HRTEM image (Fig. 3d) displays the periodic fringes of UGF, CNTs and NiO nanosheets. The inset images in Fig. 3d show that the adjacent lattice fringes are 0.20 nm and 0.24 nm corresponding to the (111) and (200) lattice planes of spinel NiO. TEM images of (a) UGF, (b) UGF/CNTs, and (c and d) UGF/CNTs/NiO composite. Corresponding (e) SAED pattern and (f) EDS spectrum of the UGF/CNTs/NiO composite. Inset in (b) shows a high-magnification TEM image of CNTs. Inset in (d) shows the corresponding high-magnification TEM images of marked area in (d).

diffraction peaked around 26.5° is the characteristic peak of carbon (UGF/CNTs), while the diffraction peaks at 37.2°, 43.5°, and 62.3° matched well with the crystal planes of the (111), (002) and (312) of NiO (JCPDS card no. 04-0835) as reported previously.27,49 The relative broad diffraction peaks reveal that NiO nanosheets in UGF/CNTs/NiO composite are of relatively low crystalinity. Moreover, no impurity peaks were found in the XRD pattern, indicating that the as-synthesized samples have high phase purity. Fig. 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,\(^ {42,50-52}\) respectively. Moreover, the integrated intensity ratio between the G and 2D bands (I\(_{G}/I_{2D}\)) revealed that the UGF was composed of few layer graphene domains. In comparison with the Raman spectrum of bare nickel foam/UGF, the Raman spectrum of the 3D nickel foam/UGF/CNTs exhibited typical characteristic D, G and 2D peaks of multiwalled carbon nanotubes.22,23 Moreover, the 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 were ascribed to the characteristic modes of crystalline Ni–O lattice vibrations in the 3D nickel foam/UGF/CNTs/NiO composite.48,54

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 elements in the as-synthesized products. The survey XPS spectrum (Fig. 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 Fig. 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 were attributed to the Ni 2p\textsubscript{3/2} and Ni 2p\textsubscript{1/2} spin–orbit levels of NiO\textsuperscript{55,56} respectively. Apart from these peaks, an additional feature peak appeared at 855.7 eV as a small shoulder, which was presumably due to the presence of a small quantity of Ni\textsubscript{2}O\textsubscript{3} on the surface.\textsuperscript{55} Fig. 5c shows the deconvoluted C 1s spectra with different oxygen containing functional groups, including

![XPS spectra](image)

Fig. 5 XPS spectra of 3D nickel foam/UGF/CNTs/NiO composite: (a) survey scan, (b) Ni 2p, (c) C 1s, and (d) O 1s.
the non-oxygenated C in C—C/C—C at 284.5 eV, the carbon in C—O/C—O—C at 283.6 eV, and the carbon in C==O/C==O at 284.8 eV.42–57 Furthermore, there are two peaks at 529.4 eV and 530.7 eV for the O 1s spectrum (Fig. 5d). According to previous reports, the binding energy peak at 529.4 eV was ascribed to Ni—OH/C—O,42–57 including defective nickel oxide with hydroxyl groups absorbed on its surface. Based on the abovementioned SEM, TEM, XRD, and Raman results, the 3D nickel foam/UGF/CNTs/NiO composite with 1D quasi-aligned CNTs/NiO core–shell structure that tightly connected with nickel foam/UGF backbones has been successfully constructed, which is favorable for developing highly conductive and high-performance electrodes.

**Supercapacitor performance**

Herein, as-prepared 3D nickel foam/UGF/CNTs/NiO composite was directly used as electrode material without the introduction of any polymer binders, and its electrochemical performances were characterized by cyclic voltammetry (CV), galvanostatic charge/discharge measurements, and electrochemical impedance spectroscopy (EIS). Fig. 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:32,56,59

\[
\text{NiO} + \text{OH}^- \leftrightarrow \text{NiOOH} + e^- \tag{4}
\]

Moreover, along with the increase of scan rates from 10 to 100 mV s\(^{-1}\), the anodic peaks shifted positively while the cathodic peaks shifted negatively, which were attributed to the polarization of the electrode at the higher scan rates.60,61 Meanwhile, a linear dependence was 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\(^{-1}\) (Fig. 6b), revealing that the redox reaction of 3D nickel foam/UGF/CNTs/NiO composite in KOH electrolyte was mainly under the diffusion-controlled step.62,63 In addition, as shown in Fig. S4 (ESI†), the 3D nickel foam/UGF/CNTs/NiO composite exhibited 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 significantly enhanced capacitance due to the unique 3D structure.

To further examine supercapacitive performances, a series of charge–discharge measurements were performed on 3D nickel foam/UGF/CNTs/NiO composite electrode at various charge–discharge current densities, as shown in Fig. 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 (Fig. 6d), the specific capacitances of 3D nickel foam/UGF/CNTs/NiO composite electrode were 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, and 10 A g\(^{-1}\), respectively. The result was comparable or better than those of the reported NiO-based composite materials, such as hierarchically porous NiO nano/micro superstructures (710 F g\(^{-1}\) at 1 A g\(^{-1}\)),7 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\(^{-1}\))7,57 and 3D NiO/ultrathin derived graphene hybrid (425 F g\(^{-1}\) at 2 A g\(^{-1}\)).64 Additionally, when the charge–discharge current density was increased 20-fold from 0.5 to 10 A g\(^{-1}\), about 71% of the original capacitance was retained, demonstrating good rate performance of the 3D nickel foam/UGF/CNTs/NiO composite electrode. As shown in the Ragone plot (Fig. 6e), the power density increased from 100.6 W kg\(^{-1}\) to 2007.3 W kg\(^{-1}\) and the energy density decreased from 18.1 W h kg\(^{-1}\) to 12.4 W h kg\(^{-1}\) respectively, as the discharge current density increased from 0.5 A g\(^{-1}\) to 10 A g\(^{-1}\).

Since long cycling life is another very crucial parameter in evaluating electrode materials for supercapacitors, the cycle stability of 3D nickel foam/UGF/CNTs/NiO composite is investigated by repeating the charge–discharge test at a current density of 5 A g\(^{-1}\) in 6 M KOH solution (Fig. 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 was better than previous reports of NiO-based composites.37,28,29,57 These encouraging results show that the 3D nickel foam/UGF/CNTs/NiO composite has 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 largely attributed to the superior 3D conducting network constructed by UGF and CNTs, and the pseudocapacitive behavior of the active material (NiO nanosheets). First, the 3D nickel foam/UGF/CNTs network offers a large material/electrolyte contact area and 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 serve as the uniform nucleation sites for NiO and offer more electrochemically 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 (Fig. S5 ESI†). In addition, the good electrical conductivity of CNTs directly enhances pseudocapacitance, and the electrochemical utilization of NiO due to the extraordinarily shortened ion diffusion and transport length (Fig. S5 ESI†).
collecting substrates of nickel foam/UGF/CNTs and the NiO nanosheets, and avoid the addition of extra additives and conductive binders.

**Li-ion battery performance**

In addition to supercapacitive performance, the lithium storage properties of the 3D nickel foam/UGF/CNTs/NiO composite were also evaluated. Fig. 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 0.01–3.0 V. In the first cathodic scan curve, a shoulder at around 0.89 V and an intensive reduction peak centered at 0.51 V corresponded, respectively, to the initial reduction of NiO to metallic Ni nanoparticles, the formation of amorphous Li\(_2\)O (NiO + 2Li\(^{+}\) + 2e\(^{-}\) \(\rightarrow\) 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 shifted to 0.98 V during subsequent cycles, which may be due to the drastic lithium driven, structural, or textural modified cations.\(^{30,37}\) The two broad peaks located at about 1.34 and 2.24 V in the first anodic scan curve were attributed to partial decomposition of the polymeric coating on the NiO surface, and decomposition of Li\(_2\)O and oxidation of metallic nickel to NiO (Ni + Li\(_2\)O \(\rightarrow\) NiO + 2Li\(^{+}\) + 2e\(^{-}\)), respectively.\(^{30,36,37,64}\) Well-known mechanisms for the abovementioned processes are the reversible reaction of NiO + 2Li\(^{+}\) + 2e\(^{-}\) \(\rightarrow\) Ni + Li\(_2\)O and partial composition/decomposition of...
the SEI layer. Moreover, the CV curves were 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 (Fig. 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 ions into UGF/CNTs. In the first charge profile, there were three plateaus located at 0.1, 1.6 and 2.2 V, which originated 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 were highly consistent with those of CV. The initial discharge and charge capacities are 1359.4 and 963.3 mA h g$^{-1}$, respectively, demonstrating an excellent high rate performance. It should be noted that as long as the current rate reversed back to the low current rate (100 mA g$^{-1}$), the cell capacity recovered 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, high rate performance is greatly dependent on rapid ionic and electronic diffusion and transport. In our case, the 3D network structure provided 3D electron-conducting channels within the electrode, and facilitated the penetration and diffusion of electrolyte, leading to fast lithium ion transport. In addition, the thin NiO nanosheets significantly shortened 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 was negligible, which can be clearly proved by its specific capacity value at different current densities (Fig. S6 ESI†).

Fig. 7d displays the cycling performance of the 3D nickel foam/UGF/CNTs/NiO composite at a current density of 200 mA g$^{-1}$. The electrode still maintained 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, hollow NiO nanotubes with a capacity of 600 mA h g$^{-1}$ at 200 mA g$^{-1}$ after 100 cycles, mesoporous NiO nanosheet networks with a capacity of 1043 mA h g$^{-1}$ at 0.2 C after 80 cycles, NiO nanosheets/graphene composite with a
capacity of 1000 mA h g\(^{-1}\) after 50 cycles 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,\(^{44}\) NIO-Ni/natural graphite with a capacity of 532 mA h g\(^{-1}\) at 0.15 C after 100 cycles.\(^{46}\) Meanwhile, coulombic efficiency was 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 was interesting to note that the slight increase and then reduction in specific capacity from 2nd cycle to 55th cycle may be due to reversible growth of a polymeric gel-like layer originating from kinetically activated electrolyte degradation and interfacial lithium storage, which is common for most anode materials.\(^{36,36}\)

Based on previously discussed 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 rationally designed nanostructure and composition. Specifically, the 3D network structure, created by CNTs/NIO core–shell nanorods growth on the 3D nickel foam/UGF, enabled sufficient electrode/electrolyte contact area for high Li\(^+\) ion flux across the interface and reduced Li\(^+\) ion diffusion length, which promoted 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 via a two-step process comprised of chemical vapor deposition and subsequent electrodeposition. The as-obtained 3D nickel foam/UGF/CNTs/NIO composite can be used as a binder-free electrode for supercapacitors and LIBs. The unique architectures, structures and morphologies have advantages such as excellent electrical contact between active materials and current collector, numerous active reaction sites and a facile ion diffusion path provided by the large open spaces between neighboring CNTs/NIO core–shell nanorods, and significantly reinforced mechanical strength, enabling their promising performance in supercapacitors and LIBs. 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\(^{-1}\), an 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 mA h g\(^{-1}\) at a current density of 100 mA g\(^{-1}\), retaining 100.9% of the initial discharge capacity after 100 cycles at 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 for use in high-performance supercapacitors, LIBs or catalysts because of their unique structural features.

Notes and references
