Hierarchical Carbon Nanofibers@Nickel Phosphide Nanoparticles for High-Performance Supercapacitors

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The design and synthesis of novel active materials as the capacitor electrodes is of great significance to fabricate high-performance supercapacitors, namely those with large and stable capacitances as well as high power and energy densities. Herein, binder-free and hierarchical carbon nanofibers@nickel phosphide nanoparticles are grown in a chemical vapor deposition reactor, where Ni$_2$TiO$_3$ nanowires and a TiO$_2$ outer layer are in situ converted into interconnected nickel phosphide nanoparticles and a TiC layer, respectively. The initially formed hierarchical nickel phosphide nanoparticles boost the catalytic growth of CNFs, leading to the generation of a 3D interconnected texture, which features a high specific surface area and excellent conductivity. The combination of this nanocomposite as a capacitor electrode with redox electrolyte of 0.05 m Fe(CN)$_6^{3-}$/$4^-$ generates a specific capacitance of 59.3 mF cm$^{-2}$ at a current density of 5 mA cm$^{-2}$. This capacitor electrode exhibits 95% of its initial capacitance even after 10 000 charging/discharging cycles. The as-fabricated supercapacitor device offers an energy density of as high as 27.4 Wh kg$^{-1}$ accompanied with a power density of 7.25 kW kg$^{-1}$. The proposed method thus provides an approach to produce binder-/current-collector-free capacitor electrodes, which can be utilized to fabricate high-performance supercapacitors.

1. Introduction

Advanced energy systems are highly required to overcome the imminent depletion of fossil fuels and ever-increasing energy demands. Among the various energy systems, supercapacitor (SC), also called electrochemical capacitor is one of the most commonly used electrochemical energy storage devices. Depending on the working mechanisms to store electrical energies, SC can generally be divided into two types: electrical double layer capacitor (EDLC) or pseudocapacitor (PC). The former stores charges through fast ion adsorption/accumulation at the electrolyte/electrode interface, while the latter involves Faradaic processes at the electrode surface. For practical applications of SCs, they are expected to own both high power and energy densities. To fabricate such high-performance SCs, the selection of suitable capacitor electrodes is of essential importance.

In this regard, various kinds of capacitor electrodes have been designed and developed. Among different capacitor electrodes, carbon nanomaterials have been extensively utilized, stemming from their low weights, excellent stability, high specific surface areas, high aspect ratios, and good electrical conductivities. Taking 1D carbon nanofibers (CNFs) as an example, they allow the electrolytes to be diffused more easily, stemming from their highly accessible specific areas. Many techniques have been then developed to synthesize 1D CNFs, including arc-discharge, laser-ablation, solvothermal and chemical vapor deposition (CVD). Among them, a CVD method has been primarily applied to synthesize 1D CNFs. This is because during a CVD process the CNFs can be grown on a desirable or suitable substrate. In this context, post-treatments of CNFs, the introduction of extra current collectors and the use of organic binders are not necessary. In other words, as-prepared CNFs can directly be applied as binder- and current-collector-free capacitor electrodes to fabricate SCs. This is fully different from other powder-like carbon nanomaterial-based capacitor electrodes, where these powders often need to be first mixed with organic binders (mostly polymers) and then pressed onto a conductor/support (namely a current collector). Unfortunately, these binders generally possess low conductivities and poor stability. The formed carbon inks (in most cases) are frequently stripped off from the current collectors underneath. Therefore, the fabricated SCs with 1D CNFs grown using a CVD approach are expected to feature big/stable capacitances and further high power/energy densities.

To grow such 1D CNFs by means of a CVD technique, a catalyst from a transition metal (e.g., Co, Ni, Fe, and Cu) is usually employed. In terms of the used substrates to grow 1D CNFs, 3D porous substrates (e.g., Ni or Cu foams) are often
employed. This is because these CNF/foam composites own increased accessible surface areas, well meeting the requirements of the capacitor electrodes to fabricate high-performance SCs. However, these 3D porous metal foams usually suffer from their low volumetric energy densities, which are caused by their low packing densities. Although the minimization of large and unused pore space inside metal foams can form their rational and tunable porose microstructures (e.g., optimal porosities and pore sizes), such fabrication processes are complex and expensive, hindering the application of conventional metal foams for the construction of SCs.\(^\text{[17]}\) Alternatively, transition metal nanoparticles loaded onto cheap and widely available substrates have been utilized as 3D porous substrates.\(^\text{[19]}\) For example, these transition metal nanoparticles can be electrochemically deposited (namely reduced from aqueous solutions) on a Si substrate. On the transition metal nanoparticle-based catalysts, the growth of 1D CNFs can be achieved. Since such growth is strongly dependent on the type, density, diameter, and thickness of these nanoparticles, the properties of 1D CNFs or the growth of 1D CNFs can be tuned through employing different catalysts.\(^\text{[18]}\) Once the density of 1D CNFs is increased, the overall accessible surface area of an electrode will be enhanced, leading to its improved electrochemical performance. Unfortunately, the agglomeration of these nanoparticles is hard to be controlled by means of this cost-effective and easily handled method (e.g., electrochemical deposition). The channels of anodic alumina have been also utilized to load metal catalysts and further applied to grow 1D CNFs.\(^\text{[19]}\) However, such a template method consists of multiple steps and is time consuming.

In this work, we report on the growth of 1D CNFs by means of a microwave plasma-enhanced CVD (MWCVD) technique as well as the utilization of these 1D CNFs as capacitor electrodes to construct high-performance SCs. In the first part of this contribution, the characterization and growth mechanism of hierarchical CNFs@nickel phosphide nanoparticles are discussed. After revealing the capacitive performance of this nanocomposite, its integration with redox electrolytes to fabricate redox-electrolyte-enhanced SCs is shown, where the capacitance, capacitance retention, energy and power densities of these SCs are detailed. In the last part of this contribution, the fabrication of a stand-alone demonstrator and its practical applications are described.

### Figure 1
Figure 1. Schematic illustration of synthesis of the composite of CNFs@nickel phosphide nanoparticles on a Ti substrate. The terms of PEO and CVD stand for plasma electrolytic oxidation and CVD, respectively.

### 2. Results and Discussion

The synthesis of hierarchical CNFs@nickel phosphide nanoparticles consists of three steps (Figure 1). In the first step, framework-like 1D ceramic Ni\(_5\)Ti\(_2\)O\(_7\) nanowires (namely a Ni\(_5\)Ti\(_2\)/TiO\(_2\) nanocomposite) are formed on a Ti substrate by means of a plasma electrolytic oxidation (PEO) method.\(^\text{[20]}\) These nanowires are then employed as the template, the support, and the precursor during a MWCVD process, when the nickel phosphide nanoparticles are initially formed. With an interconnected microstructure, these nanoparticles serve as the catalysts for the growth of 1D CNFs. Simultaneously, the existing TiO\(_2\) layer is in situ and partially carbonized to a highly conductive TiC layer, directly located beneath 1D CNFs. This nanocomposite (supported on the Ti substrate) thus fits well the requirements of a capacitor electrode (e.g., an extremely high surface area and a high conductivity, long-term stability) that are needed to construct high-performance SCs.

Scanning electron microscopy (SEM) images of a Ni\(_5\)Ti\(_2\)/TiO\(_2\) nanocomposite were recorded before and after the CVD treatment. The comparison of these images reveals the morphology variation of this nanocomposite. Before the CVD treatment, the Ni\(_5\)Ti\(_2\)O\(_7\) nanowires are needle-like and densely cover the Ti surface at varied angles (Figure 2a). The measured diameters of these nanowires are in the range of 61–226 nm. From the cross-sectional SEM image of these nanowires, one can clearly see the formation of these as-grown nanowires into a layer (Figure 2b). These nanowires are straight and their surfaces are smooth. It has been demonstrated that the Ni\(_5\)Ti\(_2\)O\(_7\) nanowires are actually grown on a TiO\(_2\) layer (namely a Ni\(_5\)Ti\(_2\)/TiO\(_2\) composite), where phosphorus ions are incorporated into during the PEO process.\(^\text{[20,21]}\) After the application of the CVD treatment in a gas mixture of CH\(_4\) and H\(_2\) for 45 min, the abovementioned features of the Ni\(_5\)Ti\(_2\)O nanowires disappear. Some new fibrous nanostructures or nanofibers appear and densely cover the Ti surface. Their diameters are in the range of 31–210 nm. Note that, the CVD treatment time determines the features of these nanofibers (Figure 2c, Figure S1, Supporting Information). For example, the application of a prolonged CVD treatment time (e.g., 2 h) reduces the surface coverage of these CNFs on the surface, probably due to the etching and dissolution of as-formed nanofibers.
under the long-term exposure of the CNFs to the plasma. In the cross-sectional SEM image of this newly formed nanocomposite (Figure 2d), two layers are clearly visible. The 1D nanofibers seem to be directly grown from the outer layer. The estimated average thickness of these nanofibers is about 3.9 μm, while that of the inner layer is about 30 μm (Figure S2, Supporting Information).

The structure of these nanofibers was further investigated. In a representative SEM image (Figure 3a), the clusters are found. Interestingly, these 1D nanofibers are directly grown on the ball-like nanoparticles (Figure 3b), which are located at either the top, the middle or the bottom of these nanofibers (Figure S3, Supporting Information). The varied distribution of these nanoparticles on the nanofibers is believed to originate from different growth modes of these nanofibers, as proposed in the vapor–liquid–solid (VLS) growth mechanism.[22–24] They are associated with the modes of tip growth, symmetrical growth, and base growth, respectively. Higher-magnification SEM images of these 1D nanofibers were then recorded with an in-lens mode, where the nanoparticles are emerged as bright spots. The elements at the nanoparticles and at the surface of a nanofiber were analyzed by means of energy-dispersive X-ray spectroscopy (EDX). The EDX spectrum of the nanoparticle (point 1) mainly exhibits the signals of Ni and P (Figure 3c), while that of a nanofiber is mainly composed of the C signal (Figure 3d). Therefore, 1D CNF is grown on the surface of nickel phosphide nanoparticles.

To examine its crystalline structure and phase of the nanocomposite obtained after the CVD treatment of the Ni₅TiO₇/TiO₂ nanocomposite, its X-ray diffraction (XRD) patterns were recorded (Figure 4a). A dome peak that appears in a low 2θ angle range indicates the formation of an amorphous carbon phase. The formed rutile TiO₂ phase (PDF#21-1276) dominates the entire diffraction pattern. This is because the rutile TiO₂ layer formed during the PEO process is extremely thick. In addition to those peaks, there are strong peaks visible at 35.9°, 41.7°, and 76.2°, which are associated with a cubic TiC phase (PDF#65-8417). The strong peak that appears at 26.4° corresponds to the (002) plane of crystalline graphite (PDF#08-0415).[25] The diffraction peaks that are centered at 44.4°, 51.7°, and 76.1° result from the metallic Ni substrate (PDF#65-0380), while those at 31.6°, 36.4°, 42.6°, and 46.6° are from nickel phosphide (e.g., Ni₃P, PDF#89-4748). Meanwhile, Raman spectroscopy was used to confirm the growth of CNFs during the CVD treatment of the Ni₅TiO₇ nanowires. In the Raman spectrum of an as-formed nanocomposite (Figure 4b), two major characteristic carbon peaks are found at about 1350 and 1600 cm⁻¹. They obviously correspond to D-band and G-band of a carbon material, respectively. Furthermore, the X-ray photoelectron spectroscopy (XPS) spectrum of this nanocomposite (Figure 4c) was recorded to detect its composition and chemical bonding states. In its XPS survey spectrum, the dominant element is carbon (87.5 at %), an indication of the successful carbonization of a Ni₅TiO₇/TiO₂ composite and the growth of CNFs during the
CVD treatment. The high-resolution C1s XPS spectrum of this nanocomposite was deconvoluted into three peaks (Figure 4d). The peaks at 284.4 and 285.6 eV are ascribed to sp²- and sp³-hybridized carbon, respectively. The C1s peak at 281.9 eV is attributed to carbon bonded to metal, confirming the formation of a metal carbide phase (here Ti–C) inside this nanocomposite.\[26\] In the high-resolution Ni2p XPS spectrum (Figure 4e), the dominating peaks are centered at binding energies of 852.8 and 853.6 eV. They correspond to Ni\(^{\delta} (0<\delta<1)\) and Ni\(^{I/II}\) in nickel phosphide, respectively.\[27\] The broad peak at \(\approx859.3\) eV can be assigned to the shake-up satellite peak of Ni2p\(_{3/2}\). In the high-resolution P2p XPS spectrum (Figure 4f), the signal with a binding energy at 129.8 eV can be ascribed to nickel phosphide (e.g., Ni–P).\[28\] These results confirm the formation of a nanocomposite of CNFs@nickel phosphide nanoparticles. This nanocomposite is expected to be electrochemically active, stemming from the presence of active nickel metal centers.

In order to describe the growth mechanism of this nanocomposite of CNFs@nickel phosphide nanoparticles on a Ti substrate, the role of H\(_2\) during the CVD treatment of the Ni\(_5\)TiO\(_7//\)TiO\(_2\) composite was clarified. When the Ni\(_5\)TiO\(_7//\)TiO\(_2\) composite is treated only in H\(_2\) atmosphere (without CH\(_4\)) for 10 min, these straight Ni\(_5\)TiO\(_7\) nanowires are converted to nanoparticles (Figure 5a). Their average diameters are varied from 87 to 262 nm. These nanoparticles are interconnected with each other, leading to the formation of a 3D network. Their surfaces are smooth (the inset in Figure 5a). More importantly, no CNFs are observed. This morphological transformation under such a condition is due to the occurrence of the reduction reaction of Ni\(_5\)TiO\(_7\) nanowires with H\(_2\) during the CVD treatment. Once the Ni\(_5\)TiO\(_7//\)TiO\(_2\) composite is treated in a gas mixture CH\(_4\) and H\(_2\) for 10 min, many tiny “droplets” are formed on the surface of the 3D hierarchical interconnected nanoparticles. The average diameter of these nanoparticles are varied from 30 to 70 nm (Figure 5b). The surfaces of these nanoparticles appear to be rough (the inset in Figure 5b). The application of a prolonged CVD treatment (e.g., 45 min) initializes the growth of CNFs (Figure 5c). Under these conditions, the CNFs are relatively short, but the surface of a Ni\(_5\)TiO\(_7//\)TiO\(_2\) composite is already fully covered by these CNFs. Note that, the concentration of CH\(_4\) in H\(_2\) needs to be carefully chosen and optimized. The growth of CNFs barely occurs when the CH\(_4\) concentration is very low (Figure S4a, Supporting Information). On the other hand, an inhomogeneous and cracked microstructure is formed when the CH\(_4\) concentration is too high in the gas mixture (Figure S4b, Supporting Information). This is because the purged H\(_2\) is used to activate and maintain the plasma. Consequently, the CNFs are assumed to grow on these tiny “droplets,” which are located on the surface of the interconnected nickel phosphide nanoparticles (the inset in Figure 5c). Since nickel phosphide nanoparticles absorb carbon species from the surrounding vapor, the accumulation of carbon atoms occurs on these “droplets.” Once these “droplets” are saturated with carbon species, the growth of CNFs starts.

Figure 3. a) SEM image of a CNF that is grown on a nickel phosphide nanoparticle, b) enlarged SEM image of a CNF, c,d) EDX spectra of the “point 1” and “point 2” in (b). The EDX signals from the Cu support were filtered.
Based on these experimental results, we hypothesize that the growth of the nanocomposite of CNFs@nickel phosphide nanoparticles occurs as follows. During the PEO treatment, the phosphorus ions are incorporated into the Ni$_5$TiO$_7$/TiO$_2$ composite and further serve as the phosphorus source to form nickel phosphide. At an initial stage of the CVD treatment, namely when only H$_2$ is introduced into the MWCVD reactor, the Ni$_5$TiO$_7$ nanowires are cracked and/or reduced by H$_2$. Since a Ni$_5$TiO$_7$
phase can be stoichiometrically considered as SnO·TiO₂, metallic Ni atoms are then formed during this process, following the reaction of NiO + H₂ → Ni + H₂O. Simultaneously, incorporated phosphate ions in the Ni₃TiO₇/TiO₂ composite are decomposed into phosphorus atoms. Their reaction with as-formed metallic Ni atoms leads to the generation of nickel phosphide nanoparticles. This is in line with the Ni—P phase diagram, where the phosphating process of metallic nickel occurs easily at high temperatures.²⁰ This statement is further supported by the related XRD patterns (Figure S5, Supporting Information) and the results shown in previous reports.²⁹⁻³⁰ For example, in addition to Ti and TiO₂ phases, the characteristic peaks of nickel phosphide (Ni₁₂P₃, PDF#65-1623) are observed after the CVD treatment of a Ni₃TiO₇/TiO₂ composite even only in H₂ atmosphere. Once the CH₄ gas is introduced into the MWCVD chamber, these nickel phosphide nanoparticles can act as the catalysts and boost the growth of CNFs. In short, the growth mechanism of the nanocomposite of CNFs@nickel phosphide nanoparticles from a phosphorus-contained Ni₃TiO₇/TiO₂ composite in a MWCVD reactor using a mixture of H₂ and CH₄ consists of the following reactions and steps: i) dissociation of CH₄ into hydrocarbon ions and radicals with aid of the H₂ plasma; ii) carbonization of the superficial TiO₂ layer by as-formed hydrocarbon species;³¹ namely the formation of a TiC outer layer and a TiO₂ inner layer; iii) the formation of nickel phosphide nanoparticles from reduced nickel and phosphorus atoms; iv) catalytic growth of CNFs on the surface of hydrocarbon species that are absorbed nickel phosphide nanoparticles. Within a proper reaction time, a multilayered nanocomposite of CNFs@nickel phosphide nanoparticles is finally formed.

It has to highlight here that the structure of a Ni₃TiO₇/TiO₂ composite plays a key role in ensuring a high specific surface of the nanocomposite of CNFs@nickel phosphide nanoparticles. The Ni₃TiO₇/TiO₂ composite is already known to possess a needle-like nanosctructure since it consists of straight and smooth nanowires.²⁰ During the conversion of these nanowires into 3D interconnected nanoparticles, the agglomeration of nickel phosphide nanoparticles and CNFs has been prevented. The Ni₃TiO₇/TiO₂ composite is thus a desirable and suitable precursor for the growth of nickel phosphide nanoparticles and CNFs. Consequently, the nanocomposite of CNFs@nickel phosphide nanoparticles is expected to offer a remarkably high and ion-accessible surface area.

The capacitive performance of the nanocomposite of CNFs@nickel phosphide nanoparticles was then examined. Prior to such measurements, electrochemical properties of this nanocomposite were studied in 1.0 m Na₂SO₄ aqueous solution (Figure S6, Supporting Information). As control experiments, electrochemical properties of a composite that was fabricated in H₂ atmosphere and a composite that was fabricated in a gas mixture of H₂ and CH₄ for 10 min were investigated. In their cyclic voltammograms (CVs), the redox waves of nickel phosphide are seen.²⁹⁻³² In contrast, the CV of the nanocomposite of CNFs@nickel phosphide nanoparticles is quasi-rectangular, where no redox activity of nickel phosphide is found. The disappearance of redox waves of nickel phosphide indicates a full coverage of nickel phosphide nanoparticles with thick CNFs. Note that, the current magnitude of the nanocomposite of CNFs@nickel phosphide nanoparticles is much smaller than that of other two composites. Since both composites exhibit redox activity of nickel phosphide nanoparticles, their PC performance was tested. Unfortunately, their capacitance retention is very poor. For example, after the application of the charging/discharging process at a current density of 20 mA cm⁻² for

Figure 5. SEM images of a Ni₃TiO₇/TiO₂ composite film after the CVD treatment a) in H₂ atmosphere for 10 min, b) in H₂ and CH₄ atmosphere for 10 min, and c) in H₂ and CH₄ atmosphere for 45 min. The insets are the related SEM images with high magnifications. The insets in (a–c) are SEM images of a Ni₃TiO₇/TiO₂ composite film with a high magnification, a representative nanoparticle (pink), and a CNF (green), respectively.
10 000 cycles, their capacitances are dramatically reduced. The deterioration of as high as 98% and 83% of their initial capacitance are found for the composites obtained in H2 atmosphere and in a gas mixture of H2 and CH4, respectively (Figure S7, Supporting Information). This is probably because of poor stability of nickel phosphide nanoparticles or facile oxidation ability of nickel phosphide nanoparticles.\(^{29,30}\) Therefore, only the nanocomposite of CNFs@nickel phosphide nanoparticles was employed in this work to fabricate SCs.

The EDLC performance of the nanocomposite of CNFs@nickel phosphide nanoparticles was examined through recording its CVs and galvanostatic charging/discharging (GCD) curves in 1.0 M Na2SO4 aqueous solution. Within a potential range of 0.1–1.1 V, the CVs recorded at different scan rates have the quasirectangular shape (Figure 6a). The calculated capacitances are 3.7, 3.4, 3.1, and 3.0 mF cm\(^{-2}\) at the scan rates of 10, 20, 50, and 100 mV s\(^{-1}\), respectively. Meanwhile, the GCD curves of this nanocomposite recorded at different current densities (Figure 6b) exhibit nearly perfect triangle or mirror-like shape. The estimated capacitances are 2.1, 2.2, 2.4, 2.6, and 3.2 mF cm\(^{-2}\) at the current densities of 5.0, 2.0, 1.0, 0.5, and 0.2 mA cm\(^{-2}\), respectively. These values indicate excellent reversibility of the nanocomposite of CNFs@nickel phosphide nanoparticles as a capacitor electrode.

It has been proved that the addition of soluble redox electrolytes into the solution can enhance the capacitance of an electrode.\(^{110}\) The capacitance enhancement of the nanocomposite of CNFs@nickel phosphide nanoparticles was then tried using this strategy. Here, 0.5 M Fe(CN)\(_6\)^{3−/4−} that was dissolved in 1.0 M Na2SO4 was used. In the CVs of the nanocomposite of CNFs@nickel phosphide nanoparticles recorded in this solution, a pair of redox peaks is seen at all scan rates (Figure 6c), obviously due to the redox reaction of Fe(CN)\(_6\)\(^{3−/4−}\) species. Taking one CV recorded at a scan rate of 50 mV s\(^{-1}\) as an example, the oxidation peak is located at 0.55 V, while the reduction peak is at 0.06 V.

The estimated capacitances of this nanocomposite in this redox electrolyte are 23.0, 35.4, 61.6, and 89.0 mF cm\(^{-2}\) at the scan rates of 100, 50, 20, and 10 mV s\(^{-1}\), respectively. They are approximately one order higher than those obtained at the same scan rates in 1.0 M Na2SO4. Meanwhile, the GCD curves of this nanocomposite in this redox electrolyte were recorded at varied current densities (Figure 6d). The plateaus in these GCD curves reflect the involvement of faradaic processes, in line with the CVs recorded at different scan rates. The estimated capacitances are 59.3, 26.9, 16.5, and 10.8 mF cm\(^{-2}\) at the current densities of 5, 10, 15, and 20 mA cm\(^{-2}\), respectively.

The capacitance retention or cycling stability of this nanocomposite was then checked in both 1.0 M Na2SO4 and 0.05 M Fe(CN)\(_6\)^{3−/4−} + 1.0 M Na2SO4 solutions. In both solutions, this nanocomposite exhibits stable capacitances (Figure 6e), as estimated from related GCD curves. For example, this nanocomposite retains 95% of its initial capacitance after 10 000 charging/discharging cycles at a current density of 5 mA cm\(^{-2}\) in 1.0 M Na2SO4 solution. In 0.05 M Fe(CN)\(_6\)^{3−/4−} + 1.0 M Na2SO4 solution, its capacitance remains 92% of its initial value after 10 000 charging/discharging cycles at a current density of 35 mA cm\(^{-2}\). Compared with that of a TiC/nickel phosphide capacitor electrode,\(^{30}\) the capacitance retention of this nanocomposite is significantly improved. Such improved capacitance retention is due to enhanced stability of this nanocomposite. Namely, the coverage of CNFs on nickel phosphide nanoparticles greatly improves the stability of this nanocomposite.

The power and energy densities of related SCs in both 1.0 M Na2SO4 solution and 0.05 M Fe(CN)\(_6\)^{3−/4−} + 1.0 M Na2SO4 solution were calculated using a symmetric two-electrode system. The mass of a capacitor electrode was estimated by weighing the nanocomposite peeled from the Ti substrate. These densities were further drawn into the Ragone plot (Figure 6f). The maximal energy density of an EDLC device (namely obtained in 1.0 M Na2SO4 solution) is 3.6 Wh kg\(^{-1}\) accompanied with a power density of 636 W kg\(^{-1}\). In 0.05 M Fe(CN)\(_6\)^{3−/4−} + 1.0 M Na2SO4 solution, the maximal energy and power densities are 27.4 and 7.25 kW kg\(^{-1}\), respectively. The power and energy densities of these SCs are comparable to those of most of traditional capacitors, other SCs, and batteries.\(^{133}\) Such high-performance stems from unique features of this nanocomposite, which is binder-free and extremely stable as well as owns a big accessible area. Therefore, such redox-electrolyte-enhanced SCs are highly promising for various applications.

To demonstrate the potential applications of the nanocomposite of CNFs@nickel phosphide nanoparticles as the capacitor electrode, a supercapacitor demonstrator was constructed. A single symmetric cell was connected to drive the red light-emitting diode (LED) with a working voltage of 1.6 V (Figure S8, Supporting Information). The integrated device can power one red LED for about 4 s after the cell is charged from +1.4 to +3.0 V. This charge–discharge process is highly reversible, as confirmed from the recorded voltage–time curve (Figure 7). Consequently, the nanocomposite is a suitable candidate as the capacitor electrode to fabricate high-performance SCs.

3. Conclusion

A novel nanocomposite of CNFs@nickel phosphide nanoparticles has been converted from the phosphorus-contained Ni3TiO7/TiO2 composite during the CVD treatment, when nickel phosphide nanoparticles are in situ formed and act as the catalysts for the subsequent growth of 1D CNFs. Meanwhile, the outer part of a TiO2 layer is carbonized to a highly conductive TiC layer. Such a binder-free and highly conductive nanocomposite thus features superior capacitive properties in both inert and redox-electrolyte-contained solutions. It can be further utilized to fabricate high-performance SCs. The strategy proposed in this study can be applied to replace traditional transition metal foams, without sacrificing their accessible surface areas. Moreover, it allows to produce the capacitor electrodes without binders or extra current collectors. However, novel approaches (e.g., by use of thermal CVD) still need to be developed to avoid the strong “etching-effect” of the plasma during the growth of CNFs on other kinds of transition metal phosphides. Meanwhile, new SCs need to be ensembled using different redox electrolytes in aqueous or organic media. The integration of these newly designed composite electrodes with novel redox electrolytes is expected to result in improved performance of these SCs (e.g., capacitances, capacitance retention, and power and energy densities) under different charging/discharging conditions. In summary, this work provides new insights for the development of
Figure 6. a,b) CVs and c,d) GCD curves of the nanocomposite of CNFs@nickel phosphide nanoparticles in a,c) 1.0 M Na$_2$SO$_4$ solution and b,d) 0.05 M Fe(CN)$_6^{3-/4-} + 1.0$ M Na$_2$SO$_4$ solution; e) Capacitance retention of the nanocomposite of CNFs@nickel phosphide nanoparticles in 1.0 M Na$_2$SO$_4$ solution (black) at a current density of 5 mA cm$^{-2}$ and in 0.05 M Fe(CN)$_6^{3-/4-} + 1.0$ M Na$_2$SO$_4$ solution (red) at a current density of 35 mA cm$^{-2}$; f) Comparison of Ragone plots of the nanocomposite of CNFs@nickel phosphide nanoparticles based SCs in 1.0 M Na$_2$SO$_4$ solution (red) and in 0.05 M Fe(CN)$_6^{3-/4-} + 1.0$ M Na$_2$SO$_4$ solution (violet) with those of traditional capacitors, other SCs, and batteries. Reproduced with permission.[33] Copyright 2008, Nature Publisher.
advanced 1D carbon nanomaterials for the construction of high-performance SCs. Stemming from superior performance of these SCs, they are promising to be used in diverse fields for different applications such as emergency power supplies and hybrid electric vehicles.

4. Experimental Section

**Synthesis and Characterization of the Composites:** The synthesis process of the nanocomposite of CNFs@nickel phosphide nanoparticles consisted of three steps, where the phosphorus-contained TiO$_2$/Ni$_5$TiO$_7$ composite acted as the precursor. The production of the phosphorus-contained Ni$_5$TiO$_7$ nanowires was conducted using a previously reported approach.[21] Briefly, the PEO method was applied to generate the TiO$_2$/Ni$_5$TiO$_7$ composite on a Ti substrate, followed by impregnation and annealing. Trisodium phosphate (Na$_3$PO$_4$) was used as both the electrolyte and the phosphorus source. To grow CNFs, the phosphorus-contained TiO$_2$/Ni$_5$TiO$_7$ composite was treated in a MWCVD reactor (ASTeX A5000). The carbon source was a methane precursor. To activate the plasma, hydrogen (H$_2$) gas with a flow rate of 400 sccm was first introduced into the MWCVD reaction chamber. Once the gas pressure was reached 45 Torr and the microwave power was 1400 W, methane was purged at a varied flow rate (e.g., from 10 to 20 sccm). The temperature on the substrate surface was measured with an infrared thermometer. It was varied from 650 to 850 °C during the CVD treatment.

The morphologies of the investigated composites were investigated using the field-emission scanning electron microscopy (FESEM, Zeiss ultra 55). The elemental compositions of the investigated composites were analyzed by means of XPS (Surface Science Instruments, SSX-100 S-probe photoelectron spectrometer) using Al K$_x$ radiation of 200 W. The high-resolution XPS spectra were recorded with a 0.1 eV-energy resolution and a spot size of 300 μm$^2$. The phase compositions of the investigated composites were determined through X-ray diffraction (XRD, Philips X’ Pert) measurements using Cu K$_x$ radiation in the 2θ range from 20° to 80° with a step of 0.05° (40 kV, 40 mA). A homemade confocal Raman spectrometer equipped with a 532 nm laser was used to record Raman spectra of the studied samples.

**Electrochemical Measurements:** Electrochemical measurements were carried out on an electrochemical workstation (CHI660E, Shanghai Chenhua Inc., China). A standard three-electrode configuration was generally applied to investigate the capacitive performance of as-synthesized composites. It consisted of an Ag/AgCl (saturated 3 M KCl) reference electrode and a Pt counter electrode. The as-prepared composite was applied directly as the working electrode since the investigated composites were directly grown on a Ti substrate. The geometric area of such a working or capacitor electrode was fixed into 0.05 cm$^2$. Cyclic voltamograms (CV) and galvanostatic charging/discharging (GCD) curves of as-fabricated capacitor electrodes were recorded at different scan rates and current densities, respectively. The GCD technique was also employed to check the cycling stability of as-formed SCs. Both EDLCs and redox-electrolyte-enhanced SCs were fabricated. To fabricate EDLC, the used electrolyte was 1.0 M Na$_2$SO$_4$ aqueous solution, while the redox-electrolyte-enhanced SCs were fabricated using 0.05 M K$_3$Fe(CN)$_6$/K$_4$Fe(CN)$_6$ dissolved in 1.0 M Na$_2$SO$_4$. To estimate the energy and power densities of as-formed SCs, a two-electrode system was applied. A 50-μm-thick Nafion membrane (Alfa Aesar, Germany) was used as the separator. The specific capacitances (C, F cm$^{-2}$), energy densities ($E, W h kg^{-1}$), and power densities ($P, W kg^{-1}$) of these SCs were calculated according to the reported methods.[14] SC Demonstrators: A similar electrical configuration to those reported[19] was applied to fabricate a stand-alone and USB-chargeable demonstrator. Two nanocomposites of CNFs@nickel phosphide nanoparticles were symmetrically assembled on both sides of a cell. With a 50-μm-thick Nafion membrane as a separator, the cell was separated. The electrolytes of both 1.0 M Na$_3$PO$_4$ aqueous solution and 0.05 M K$_3$Fe(CN)$_6$/K$_4$Fe(CN)$_6$ dissolved in 1.0 M Na$_2$SO$_4$ were applied.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords

carbon nanofibers, composites, energy densities, nickel phosphide, supercapacitors

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