**Dilute NiO/carbon nanofiber composites derived from metal organic framework
fibers as electrode materials for supercapacitors**

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Abstract

A new type of carbon nanofiber (CNF) dominated electrode materials decorated with dilute NiO particles (NiO/CNF) has been *in situ* fabricated by direct pyrolysis of Ni, Zn-containing metal organic framework fibers, which are skillfully constructed by assembling different proportional $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ with trimesic acid in the presence of N,N-dimethylformamide. With elegant combination of advantages of CNF and evenly dispersed NiO particles, as well as successful modulation of conductivity and porosity of final composites, our NiO/CNF composites display well-defined capacitive features. A high capacitance of 14926 F g^{-1} was obtained in 6 M KOH electrolyte when the contribution from 0.43 wt% NiO was considered alone, contributing to over 35% of the total capacitance (234 F g^{-1}). This significantly exceeds its theoretical specific capacitance of 2584 F g^{-1} . It has been established from the Ragone plot that a largest energy density of 33.4 Wh kg^{-1} was obtained at the current density of 0.25 A g^{-1} . Furthermore, such composite electrode materials show good rate capability and outstanding cycling stability up to 5000 times (only 10% loss). The present study provides a brand-new approach to design a high capacitance and stable supercapacitor electrode and the concept is extendable to other composite materials.

Keywords: Metal organic framework; Nickel oxide; Carbon nanofiber; *In situ* synthesis; Capacitance

1. Introduction

With imminent exhaustion of fossil fuels and rapid growth of energy requirements, it is required to seek alternative energy sources and advanced energy storage devices [1,2]. Fuel cells, secondary batteries and capacitors are considered to be promising candidates for new energy systems to meet the requirement of high capability. Supercapacitors, which fill the gap between batteries and conventional electrostatic capacitors in terms of power and energy densities, are considered as a very important element of energy storage applications due to their high power density, long cycle life and fast charge-discharge rate [3]. Supercapacitors can be generally classified as electric double layer capacitor (EDLC) and pseudocapacitor based on the charge storage mechanism. EDLCs, commonly use carbon-based materials with high porosity as electrodes, showing large power density and long cycle life, but low electrochemical capacitance [4]. As for pseudocapacitors, transition metal oxides offer higher capacitance than carbon materials and better cycling stability than polymers, but suffer from a drawback of poor conductivity [5]. Considering this, it has inspired efforts to develop hybrid electrodes with transition metal oxides and porous carbons. In this case, these electrodes would show the combined advantages of EDLC and pseudocapacitor, which contributes to an enhanced capacitance of a supercapacitor. Such a hybrid supercapacitor will be widely used in the field of consumer electronics, energy management, memory back-up system, industrial power and mobile electrical systems [6-8].

To be competent for these applications, inexpensive transition metal oxides like

MnO₂, NiO, Co₃O₄, MoO₃ and V₂O₅ have been used as the pseudocapacitive components in carbon-based hybrid electrode materials [9]. Among them, NiO is one of the most promising candidates due to its high theoretical capacitance (2584 F g⁻¹), environmentally benign nature, low cost and easy preparation process. For example, composites of NiO coupled with activated carbon, graphene, carbon nanotube (CNT), or carbon nanofiber (CNF) have been intensively studied for lithium-ion batteries and supercapacitors [10-13]. To obtain a high capacitance, a significantly large proportion of NiO (> 5.0 wt%) is inevitable in these supercapacitors. It is worth mentioning that such pseudocapacitance dominated electrode materials often meet with low rate capability and poor cycling stability (less than 3000 cycles). It can be imagined that the most promising approach in supercapacitor fabrication is the development of carbon dominated electrode materials with dilute NiO decorated, which are expected to show integrated merits of large specific capacitance, excellent rate capability and high cycling stability.

Carbon nanofiber is an intriguing one-dimensional carbon material that is widely utilized to design fascinating electrode materials for supercapacitors because of its excellent electrical conductivity and mechanical stability [14]. Recently, application of CNF-based transition metal oxide composites as electrochemical materials is reported [15-17]. CNF has offered not only a conductive backbone to facilitate electron transport, but also a mechanical structure that maintains the integrity of the electrode during the electrochemical process. In these systems, metal oxides are often grafted onto CNFs using chemical stabilizers. This may damage the CNF structure

1 and decrease the conductivity, adversely affecting the capacitance. The weakly
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3 attached metal oxides may suffer from detachment during processing and application,
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6 which leads to impaired stability. Alternatively, stable metal oxide/CNF composites
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9 can be facilely prepared by electrospinning of metal salt-polyacrylonitrile fibers
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11 before a thermal conversion [18,19]. However, such facile synthesis often renders
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13 low surface area and porosity in the resulting composites, though some pore-forming
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15 agents are introduced [20-22], which decreases the electrolyte diffusion and charge
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17 transfer significantly. Therefore, fabrication of high-performance dilute metal
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19 oxide/carbon nanofiber composites remains challenging.
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25 We herein report a new type of CNF dominated electrode materials decorated
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27 with dilute NiO particles (NiO/CNF) *in situ* fabricated by direct pyrolysis of Ni,
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29 Zn-containing metal organic framework fibers, which are skillfully constructed by
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31 assembling different proportional $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ with trimesic acid
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33 in the presence of N,N-dimethylformamide. The carbon networks are decorated by
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35 evenly dispersed NiO particles, and the conductivity and porosity of final composites
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37 are tailored by varying the feed ratio of metal precursors. The elaborately fabricated
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39 NiO/CNF composite displays well-defined capacitive features. A high capacitance of
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41 14926 F g^{-1} was obtained in 6 M KOH electrolyte when the contribution from 0.43 wt%
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43 NiO was considered alone, contributing to over 35% of the total capacitance (234 F
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45 g^{-1}). And a largest energy density of 33.4 Wh kg^{-1} was obtained at the current density
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47 of 0.25 A g^{-1} . Furthermore, good rate capability and outstanding cycling stability up to
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49 5000 times (only 10% loss) were shown. The superior performance can be ascribed to
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the successful construction of dilute NiO/carbon nanofiber composites bearing high conductivity and porosity by the *in situ* synthesis.

2. Experimental

2.1. Chemicals

Zinc acetate dihydrate ($\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$, AR), nickel chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, AR), trimesic acid ($\text{C}_9\text{H}_6\text{O}_6$, > 98%, TCI), N,N-dimethylformamide (DMF, AR), nitrogen (N_2 , > 99.999%), acetylene black (Battery Grade), polytetrafluoroethylene (PTFE, 60 wt%, Aldrich), Ni foam (Battery Grade), and ethanol (AR) are all commercially received and used directly without further purification.

2.2. Synthesis of NiO/carbon nanofiber composites

Trimesic acid (H_3BTC), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ were used as precursors for Ni, Zn-containing metal organic framework fiber synthesis. In a typical synthesis procedure, 1.25 g of H_3BTC (6.0 mmol) were dissolved in 50 mL of DMF under constant agitation at room temperature for 3 min, followed by addition of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (5x mmol) and $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ (5(1-x) mmol) [x was defined as the Ni molar percentage in all metals, and was set to be 0, 0.025, 0.100 and 0.500%]. The mixture was stirred for a further 30 min. The resulting mixture was then transferred into a Teflon-lined stainless steel autoclave and heated at 140 °C for 12 h. After the autoclave was cooled to room temperature, the precursor was filtered and washed with DMF, and then dried under vacuum, yielding 100xNi-ZnBTC fibers. Afterward, the dried precursors were pyrolyzed at 950 °C for 2 h in a nitrogen atmosphere,

yielding 100xNiO/CNF composites (Scheme 1). Additionally, post-grafted NiO/CNF composite (0.100NiO/CNF-p) and mechanically mixed NiO-CNF material (0.100NiO-CNF-m) are also prepared for comparison (Supporting Information).

2.3. Characterization

2.3.1. Lab characterization techniques

Powder XRD data were measured by a Bruker D8 Advance X-ray diffractometer with nickel filtered $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The FTIR spectra were obtained on a Nicolet Nexus 870 FT-IR spectrometer from 4000 to 400 cm^{-1} at room temperature. SEM was performed on a field-emission scanning microscope (FEI-Quanta 200F) operated at 15 kV with an EDX detector. Morphologies of the detailed structures were observed with a FEI Tecnai G2 F20 transmission electron microscope (TEM), selected area electron diffractions (SAED), high angle annular dark field scanning TEM (HAADF-STEM) and elemental maps. An energy dispersive X-ray spectroscopic analyzer was equipped and operated at a voltage of 200 kV. The N_2 adsorption/desorption experiments were performed at liquid nitrogen temperature (-196°C) using a static volumetric gas adsorption instrument (JW-BK222). Before measurements, all the samples were de-gassed at 300°C for 3 h in vacuum. Specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method applied to adsorption data in the relative pressure range (P/P_0) range of 0.05-0.20. The mesopore size distributions were measured using Barrett-Joyner-Halenda (BJH) method from the desorption branch of the isotherms. The linearized BET model was used to fit the microporous data within the relative pressure range of $0.001 < P/P_0 <$

0.05. The micropore size distributions were determined using the Horvath-Kawazoe (H-K) method assuming slit pore geometry. Raman spectra were recorded using a HORIBA Jobin Yvon HR800 with a 633 nm laser.

Each 10 mg of vacuum-dried NiO/CNF composite was placed in a digester with PTFE lined, and dissolved in 4 mL of aqua fortis solution mixed with 1 mL H₂O₂. Microwave digestion was carried out for 30 min to completely dissolve nickel species. After cooling, each solution was filtered through a 0.45 µm polyethersulfone filter and then submitted for analysis. Nickel content was estimated by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis conducted on a Perkin Elmer emission spectrometer.

2.3.2. Synchrotron radiation characterization techniques

X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) experiments were performed on beamline 12-BM-B of the Advanced Photon Source at Argonne National Laboratory. XANES and EXAFS spectra were recorded for each sample in fluorescence mode at the Ni K-edge (8333.0 eV). Athena software was used for background removal, post-edge normalization and XANES analysis. The oxidation states of the samples were determined by comparing the inflection point of the edge from the sample to that of standards with known oxidation state. Artemis software was used for EXAFS analysis, which implemented FEFF. The EXAFS function, χ , was obtained by subtracting the post-edge background from the overall absorption and then normalized with respect to the edge jump step. The Fourier transformation of the k-weighted $\chi(k)$ data from k space to r space was

performed over the range of 2-11 Å⁻¹ to obtain a radial distribution function. For the curve-fitting analysis, the empirical phase shift and amplitude functions for Ni-O and Ni-Ni were extracted from the data for bulk NiO and Ni foil, respectively.

2.4. Electrochemical test

For the electrochemical measurements, the prepared sample was mixed with acetylene black and polytetrafluorethylene, in a weight ratio of 7: 2: 1. The resulting working electrode slurries were coated on the nickel foam (surface, 1 cm × 1 cm). After being dried at 60 °C for 2 h, the as-formed electrodes were then pressed at 3 MPa, and further dried at 60 °C overnight before use.

The capacitive performance of all samples was tested on a CHI660D electrochemical workstation, by employing a conventional three-electrode system with a Hg/HgO and a Pt as the reference and counter electrodes, respectively. The electrochemical properties were evaluated by cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS) in 6 M KOH-distilled water electrolyte. EIS measurements were recorded at open circuit potential with a frequency loop from 10³ kHz to 1 mHz. The CV was used to examine the performance of the supercapacitor. The specific capacitance (C_m) was calculated from the CV curves based on the following equation:

$$C_m = \frac{C}{m} = \frac{S}{2UVm}$$

Where C_m, C, m, S, V and U are the gravimetric specific capacitance (F g⁻¹), capacitance (F), mass of electrode material (g), integrated area of the CV curve, scan

rate (mV s^{-1}) and potential window (V), respectively.

The pseudocapacitance due to NiO (C_{NiO}) in the composite was calculated by subtracting the EDLC capacitance contributed by carbon nanofiber substrate according to the following equation:

$$C_{\text{NiO}} = (C_m - C_c \times C\%)/\text{Ni}\%$$

Where C_c , $C\%$ and $\text{Ni}\%$ are the specific capacitance of CNF electrode, weight percentages of CNF and NiO in the composite, respectively.

In the GCD curves, the energy density (E , J g^{-1}) and power density (P , W g^{-1}) can be calculated using the equations as follows:

$$E = \frac{1}{2} \times C_n \times (\Delta V)^2$$
$$P = \frac{E}{\Delta t}$$

Where C_n is the gravimetric specific capacitance (F g^{-1}) based on the galvanostatic charge-discharge test, ΔV (V) refers to the potential change within the discharge time Δt (s).

3. Results and discussion

3.1. Morphology of Ni, Zn-containing metal organic frameworks

First, SEM study of Ni, Zn-containing metal organic frameworks was performed to examine the formation of fiber precursors, which is the prerequisite to fabricate CNF-based composites. Figure 1a-c shows the SEM images of three Ni-ZnBTC precursors bearing different Ni molar percentages. It is clear that they have a fibrous shape with an average diameter of *ca.* 100 nm and a length of 3-10 μm . These fibers are less uniform when increasing the Ni molar percentage to 1.000% (Fig. S1). This

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3 successfully constructed *via* a self-assembly process by varying the Ni molar
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5 percentage ranging from 0.025 to 0.500%.
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8 9 **3.2. Morphology and microstructure of NiO/carbon nanofiber composites**

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11 Being pyrolyzed, the parent fibrous morphology is inherited in the resulting
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13 NiO/CNF composites (Fig. 1d-f). However, these nanofibers are slightly contracted,
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15 and their surface gets rough and fluffy. This indicates that the parent fibers are rigid
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17 and went through a decomposition when pyrolyzed, accompanied by the liberation of
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19 volatile gases including H₂ and CO. To explore the microstructure of NiO/CNF
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21 composites, TEM observation of the representative 0.100NiO/CNF was performed
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23 and the corresponding images are displayed in Fig. 2a. It is found that these
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25 nanofibers are interconnected. SAED study of these nanofibers gives diffraction rings
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27 assigned to graphitic carbons and diffraction spots ascribed to Ni-containing
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29 nanocrystalline (Fig. 2b). This implies that the Ni-containing particles are formed and
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31 are *in situ* anchored onto carbon nanofibers formed simultaneously. To gain deep
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33 insight into the 0.100NiO/CNF composite, TEM observation for a single nanofiber
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35 (Fig. 2c) and a single particle (Fig. 2d) was performed. The corresponding images
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37 show that the particles are embedded into the fibrous networks, indicating a firm
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39 contact. HAADF-STEM study reveals the presence of hollow nanofibers decorated
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41 with evenly dispersed spots (Fig. 2e), which prove to be carbon nanofiber within NiO
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43 particles by elemental mapping analysis (Fig. 2f).
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58 59 **2.5. Transformation of fiber precursors to NiO/carbon nanofiber composites**

Chemical analysis was employed to investigate the transformation of fiber precursors. The representative Ni, Zn-containing metal organic framework fiber, 0.100Ni-ZnBTC, shows stretching vibrations at 1635, 1566, 1364 and 1250 cm^{-1} in the FT-IR pattern (Fig. 3Aa), corresponding to the phenol-bridged struts. However, these vibrations disappear when pyrolyzed (Fig. 3Ab), implying the conversion of organic struts to inorganic carbons. EDS analysis of 0.100Ni-ZnBTC shows the presence of rich C, O and Zn species (Fig. S2a). Zn species are not detected in final 0.100NiO/CNF (Fig. S2b), which implies that most Zn species are removed after high-temperature pyrolysis at 950 °C for 2 h, leaving dominated carbons, in accordance with the FT-IR result.

XRD was carried out to investigate the structural transformation of 0.100Ni-ZnBTC. As displayed in Fig. 3Ba, the XRD pattern of 0.100Ni-ZnBTC shows strong diffraction peaks ranging from 5 to 20°, corresponding to the *rutile*-structured ($P4_2/mnm$) arrays [23]. The following high-temperature pyrolysis yielded 0.100NiO/CNF composite, showing (002) and (101) diffractions at 23° and 43° (Fig. 3Bb), respectively [24]. This strongly suggests the transformation of crystalline metal organic framework fibers to carbonaceous materials. Additionally, an in-plane structural sign of typical graphitic carbon at around $2\theta = 13^\circ$ is observed, indicating that the graphitic structures are well developed in 0.100NiO/CNF [25].

Investigation of the transformation for Ni-containing species is difficult using lab characterization techniques. For example, Ni species are silent using X-ray photoelectron spectroscopy since the Ni molar percentage is extremely low

(0.025-0.500%) in the synthetic mixture, and the Ni content is very dilute in final composites (0.08-0.80 wt%, Table S1). In this specific case, XAFS based on the synchrotron radiation was employed since it has high flux and intensity. As illustrated in Fig. 3C, compared with 0.100Ni-ZnBTC, 0.100NiO/CNF exhibits a pre-edge feature, a declined white line intensity and a negative shift in the adsorption edge position, suggesting the Ni species are mostly reduced during pyrolysis [26]. Whereas these reduced Ni species carry some positive charges since the edge position has a positive shift compared with Ni foil. In the corresponding k space, 0.100NiO/CNF shows weak oscillations at a higher k region of $k > 8 \text{ \AA}^{-1}$ (Fig. S3), which is similar to 0.100Ni-ZnBTC. This indicates the dominance of low Z backscatters, which would be O in our system [27]. Accordingly, the 0.100NiO/CNF exhibits a peak at 1.60 Å from Ni-O contributions [28], and another peak at 2.10 Å from Ni-Ni pairs in the Fourier transformed EXAFS (r space, Fig. 3D). Curve fitting of EXAFS data in r space demonstrates that the Ni-O pairs have a coordination number of 1.7, which is a half of that for Ni-Ni pairs, further confirming the formation of NiO particles.

2.6. Effect of feed ratio

In our experiment, the feed ratio of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ was varied, which tailored the NiO dosage in the final composite (0.10-1.01 wt%). To explore the effect of feed ratio on the carbonaceous networks, Raman spectroscopy was performed to investigate the local structure of carbons in different NiO/CNF composites. As illustrated in Fig. 4a, two major bands are observed, corresponding to the D and G bands of carbon. The G bands at around 1595 cm^{-1} can be assigned to the

1 E_{2g} phonon of C sp^2 atoms, which is mainly due to the existence of carbon atoms of
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3 the graphite phase. The D bands at around 1349 cm^{-1} is derived from a breathing
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5 mode of k -point phonons of A_{1g} symmetry, which is related to the considerable bond
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7 disorder such as the presence of five- and seven-membered rings [29]. As the overlap
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9 between D and G band, the A band at around 1504 cm^{-1} is deconvoluted and can be
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11 ascribed to heteroatom-doped amorphous carbons [30]. It is noteworthy that the
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13 integral area ratio of the "D band" to the "G band" (I_D/I_G) indicates the degree of
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15 graphitization of carbonaceous materials, and the integral area ratio of the "A band" to
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17 the "G band" (I_A/I_G) indicates the proportion of oxygen-containing groups in
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19 carbonaceous networks. To investigate the graphitization and functionalization of
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21 carbon networks, curve fitting of Raman spectra was performed to quantify I_D/I_G and
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23 I_A/I_G . As shown in Fig. 4b-d and Table S1, 0.100NiO/CNF shows the lowest I_D/I_G
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25 value of 2.37 among NiO/CNF composites, owing to the most developed graphene
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27 sheet formed when 0.43 wt% of NiO was introduced. However, the lowest I_D/I_G value
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29 is much larger than those (0.75-0.99) obtained from nickel-doped activated
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31 mesoporous carbon microsphere, in which more nickel species are involved and
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33 graphitization of pre-formed carbons are more efficient [31]. Moreover, the largest I_A/I_G
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35 value of 0.33 was obtained for 0.100NiO/CNF. The presence of a largest fraction of
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37 oxygen-containing groups in carbon networks implies a highest affinity to anchored
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39 NiO particles [32].
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55 N_2 adsorption was performed to investigate the pore structure of different
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57 NiO/CNF composites and pristine CNF. All of the isotherms exhibit an intermediate
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mode between type I and type IV (Fig. 5A and Fig. S4A). A steep increase in the adsorption was observed below the relative pressure of 0.01, followed by a moderate slope at intermediate pressures accompanied by an H₄ hysteresis loop, implying the hierarchically micro- and mesoporous arrays [33,34]. The mesopore size, calculated using the Barrett-Joyner-Halenda method, shows a mono distribution centered at *ca.* 3.6 nm; while the micropore size, estimated using the Horvath-Kawazoe method, exhibits a bimodal distribution centered at 0.9 nm (Fig. 5B and Fig. S4B). The above analysis confirms the formation of hierarchically structured NiO/CNF composites. Recent studies demonstrate that micro- and/or mesoporous carbon spheres [35-37], which have a hierarchical structure, facilitate the adsorption and transportation of electrolyte during electrochemical test. It is worth mentioning that the pore size is nearly identical for different NiO/CNF composites, implying the NiO particles are mainly inserted into the carbonaceous network, further confirming a tight contact. However, the surface area increases from 548 m² g⁻¹ for 0.025NiO/CNF to 598 m² g⁻¹ for 0.100NiO/CNF, and then decreases to 468 m² g⁻¹ for 0.500 NiO/CNF (Table S2). It is the same manner for pore volumes. This suggests that NiO dosage affects the surface area and porosity of final composites significantly. Furthermore, the microporous fraction, which is defined as V_{micro}/V_p (Table S2), also varies depending on NiO dosage. The 0.100NiO/CNF exhibits a larger V_{micro}/V_p value of 0.39 compared with other two, demonstrating more voids are created in the carbonaceous network [38].

2.7. Electrochemical property

To evaluate the electrochemical properties of NiO/CNF composites, we first carried out cyclic voltammetry (CV) measurements at the same potential sweep rate of 1 mV s⁻¹ (Figure 6a). The CV curves display the prevailing double layer effect, in addition to the pseudocapacitance behavior. These distorted and complex CV curves arise due to the double layer effect of CNF and faradic redox reaction of NiO. The pseudocapacitive oxidation reduction performance of NiO can be represented as follows:

The absence of obvious redox peaks suggests the charge-discharge is proceeded at a constant rate [39]. From the CV curves, the remarkable difference between 0.100NiO/CNF and CNF can be easily recognized. In detail, the 0.100NiO/CNF exhibits a larger rectangular curve corresponding to a higher capacitance (234 F g⁻¹) than CNF (170 F g⁻¹). This strongly suggests the critical role of NiO in the capacitance enhancement. The introduction of pseudo-capacitive NiO unambiguously increases the total capacitance, whereas, on the other hand, the microstructure improvement of CNF caused by the catalytic graphitization effect of nickel component also play a role. In this specific case, the capacitance enhancement for 0.100NiO/CNF originates from the synergism between pseudo-capacitive NiO and porous CNF. On the other hand, compared with 0.100NiO/CNF, the post-grafted 0.100NiO/CNF-p and mechanically mixed 0.100NiO-CNF-m exhibit a much lower specific capacitance of 122 and 181 F g⁻¹, respectively. The superior performance of 0.100NiO/CNF can be ascribed to the even dispersion of NiO rendered by one-pot

assembly before pyrolysis. As for NiO/CNF composites, the specific capacitance increases from 208 F g⁻¹ for 0.025NiO/CNF to 234 F g⁻¹ for 0.100NiO/CNF, and then decreases to 147 F g⁻¹ for 0.500NiO/CNF, indicating the NiO dosage affects the capacitance significantly. The dilute but optimized NiO content should be responsible for the best capacitive performance of 0.100NiO/CNF, which improves the ratio graphitic component and porous structure in a comprehensive way, leading to excellent conductivity and electrolyte ion/charge transfer during the electrochemical test. Complete leading of NiO in 0.500NiO/CNF was performed using 35 wt% HCl solution, and the largest capacitance of 178 F g⁻¹ was obtained at the scan rate of 1 mV s⁻¹ (Fig. S5), slightly larger than that using pristine CNF in the absence of NiO. Further evaluation of pseudocapacitance based on NiO (C_{NiO}) in the composite was performed. As shown in Table S3, the pseudocapacitance is 36764 and 14926 F g⁻¹ for 0.025NiO/CNF and 0.100NiO/CNF, respectively, which is larger than that of any NiO-based material [40-42], nearly 15 times of the theoretical specific capacitance of NiO (2584 F g⁻¹). It is probable that the anchored NiO is dilute and highly dispersed, and therefore can be fully used, contributing to an extremely large capacitance.

In order to further investigate the properties of our samples, GCD experiments were performed at a current density of 0.25 A g⁻¹ (Fig. 6b). These charge-discharge curves are linear and symmetrical, indicating excellent electrochemical reversibility and charge-discharge efficiency (nearly 100%). The charge storage capacity of 0.100NiO/CNF is significantly higher than that of other NiO/CNF composites with a 14-92% increase in the discharge time. The change of capacitance based on the

GCD curves is consistent with that from the cyclic voltammograms. Figure 6c displays the GCD curves of 0.100NiO/CNF obtained at different current densities ranging from 0.25 to 2.00 A g⁻¹. A good symmetry and fairly linear slope are observed, indicating a good electrochemical capacitive characteristic and superior reversible redox reaction. It reveals good rate performance, especially at large charge-discharge current densities, implying that the 0.100NiO/CNF is suitable for applications in supercapacitors in which the rapid charge-discharge is required. Additionally, negligible voltage drop (IR drop) can be seen from the GCD curves, indicating a really low internal resistance, which is important for energy storage electrodes. The power density and energy density are calculated based on the charge-discharge test, and the capacitances based on the GCD curves are listed in Table S4. Figure 6d shows the Ragone plot of 0.100NiO/CNF electrode. As the current density decreases from 2.00 to 0.25 A g⁻¹, the power density decreases from 1000 to 125 W kg⁻¹, and the energy density, on the contrary, increases from 29.0 to 33.4 Wh kg⁻¹. The largest energy density is even orders higher than that of reported electric double-layer capacitors and pseudocapacitors [43,44].

It is well-known that an ideal supercapacitor can deliver the same energy under any operation conditions. As a result, it is important to explore the capacitance retention at a higher scan rate. So CV investigation was carried out under different scan rates for 0.100NiO/CNF. As shown in Fig. 7a, even at a scan rate as high as 100 mV s⁻¹, the CV curves retain a relatively rectangular shape without a very oblique angle, indicating the superior capacitive nature [45]. The specific capacitance

decreases by 29% (from 234 to 167 F g⁻¹) as the sweep rate increases from 1 to 100 mV s⁻¹, linking to the excellent mesoporosity [46]. The relationship between the capacitance retention ratio and potential scan rate is plotted for CNF and NiO/CNF composites (Fig. 7b). A small decrease in the capacitance is observed as the scan rate goes from 1 to 10 mV s⁻¹. The capacitance retention ratios at 100 mV s⁻¹ are above 70% for all NiO/CNF composites, implying that hierarchically porous structure is suitable for quick ion transportation. However, at a high scan rate ranging from 50 to 100 mV/s, the capacitance retention ratios decreases following the sequence of 0.100NiO/CNF, 0.025NiO/CNF and 0.500NiO/CNF. This sequence is consistent with the decrease of microporous fraction in NiO/CNF composites (Table S2). The larger capacitance retention ratio of 0.100NiO/CNF may be related to the higher microporous fraction, since more micropores can provide better charge accommodations.

EIS is a powerful test that gives lots of information regarding internal resistance of the electrode and resistance between the electrode and electrolyte. Figure 7c shows the Nyquist plots for both CNF and NiO/CNF composite electrodes, which are composed of a typical semicircle in the high frequency region and a straight line at low frequency. Obviously, compared with other composites, a smaller semicircle is observed for 0.100NiO/CNF, which means smaller charge transfer resistance [47]. This indicates the higher porosity of 0.100NiO/CNF renders electron transport from NiO to CNF more efficient. The intercept of the semicircle on the real axis at high frequency represents the equivalent series resistance [48]. It is apparent that the

1 solution resistance for NiO/CNF composites is very low, smaller than $0.72\ \Omega$ except
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3 for that of 0.500NiO/CNF, suggesting the superior conductivity was achieved when
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5 the NiO dosage is no more than 0.43 wt%.
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9 Furthermore, we studied the durability of the 0.100NiO/CNF electrode using
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11 GCD test to investigate the long-term charge-discharge behavior at a current density
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13 of $5\ \text{A g}^{-1}$. As illustrated in Fig. 7d, the specific capacitance still remains at $170\ \text{F g}^{-1}$
14
15 (ca. 90% of the initial capacitance, $189\ \text{F g}^{-1}$) after 5000 cycles. The fading rate is only
16
17 0.002% per cycle, which illustrates that the 0.100NiO/CNF electrode exhibits a good
18
19 cycling and stability behavior. The cycling performance of 0.100NiO/CNF is much
20
21 better than that of pseudocapacitance dominated electrode materials, such as
22
23 nanostructured (Co, Ni)-based compounds coated on carbon nanorod arrays (ca. 11.5%
24
25 loss after 3000 cycles) [49], NiAl layered double hydroxide/multiwalled carbon
26
27 nanotube/nickel foam electrode (decreased by ca. 17% after only 1000 cycles) [50],
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29 and C@NiO electrode (ca. 10% loss after 1000 charge-discharge cycles) [51].
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39 4. Conclusions

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42 In summary, a new type of carbon nanofiber dominated electrode materials
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44 decorated with dilute NiO particles has been successfully developed by direct
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46 pyrolysis of Ni, Zn-containing metal organic framework fibers. The conductivity and
47
48 porosity of final composites optimized by varying the feed ratio of metal precursors.
49
50
51 With the elegant combination of the advantages of double layer CNF and evenly
52
53 dispersed pseudo-capacitive NiO, a high capacitance of $14926\ \text{F g}^{-1}$ was obtained,
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55 contributing to over 35% of the total capacitance ($234\ \text{F g}^{-1}$) and exceeding its
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1 theoretical specific capacitance. The largest energy density of 33.4 Wh kg⁻¹ was
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3 achieved at the current density of 0.25 A g⁻¹. Furthermore, such composite electrode
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5 materials show good rate capability and outstanding cycling stability. We anticipate
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7 that such a fabrication will be applicable to more hybrid materials and energy storage
8
9 and conversion devices such as lithium ion batteries, water splitting cells, and
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11 photodetectors.
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Figure 1

Fig. 1. SEM images of (a) 0.025Ni-ZnBTC, (b) 0.100Ni-ZnBTC, (c) 0.500Ni-ZnBTC, (d) 0.025NiO/CNF, (e) 0.100NiO/CNF and (f) 0.500NiO/CNF.

Figure 2

Fig. 2. TEM image (a), SAED analysis (b), high-magnification TEM image for a single nanofiber (c) and a single particle (d), HAADF-STEM image (e) and elemental maps (f) of 0.100NiO/CNF.

Figure 3

Fig. 3. FT-IR pattern (A), XRD pattern (B), Ni K-edge XANES (C) and Ni K-edge EXAFS (D) of (a) 0.100Ni-ZnBTC, (b) 0.100NiO/CNF and (c) Ni foil.

Figure 4

Fig. 4. Raman spectra (a) and curve fitting for samples of (b) 0.025NiO/CNF, (c) 0.100NiO/CNF and (d) 0.500NiO/CNF.

Figure 5

Fig. 5. N₂ adsorption/desorption isotherms (A) and the corresponding pore size distribution curves (B) of (a) 0.025NiO/CNF, (b) 0.100NiO/CNF and (c) 0.500NiO/CNF.

Figure 6

Fig. 6. Capacitive performance: (a) CV curves at 1 mV s^{-1} , (b) GCD curves at 0.25 A g^{-1} , (c) charge-discharge curves of 0.100NiO/CNF at various current densities and (d) Ragone plot performed in 6.0 M KOH aqueous solution for 0.100NiO/CNF.

Figure 7

Fig. 7. Capacitive performance: (a) CV curves at different scans for 0.100NiO/CNF, (b) capacitance retention ratios as a function of scan rates in 6 M KOH, (c) Nyquist plots and (d) cycling stability of 0.100NiO/CNF.

Facile construction and evolution of Ni, Zn-containing metal organic framework fibers has been designed to *in situ* fabricate dilute NiO/carbon nanofiber composites as high-performance electrode materials.