Low-Crystalline FeOOH Nanoflower Assembled Mesoporous Film Anchored on MWCNTs for High-Performance Supercapacitor Electrodes

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ABSTRACT: Crystalline iron oxides/hydroxides are generally preferred as supercapacitor electrode materials instead of the low-crystalline structure, despite the fact that an amorphous phase could have a comprehensive electrochemical performance owing to its structural disorder. Herein, we present a facile and scalable method for preparing amorphous FeOOH nanoflowers@multi-walled carbon nanotubes (FeOOH NFs@MWCNTs) composites. The resulting hybrid nanoflowers hold a distinctive heterostructure composed of a self-assembled amorphous FeOOH nanofilm on the MWCNTs surface. The low-crystalline 1FeOOH NFs@1MWCNTs composites at pH 8 exhibit a high comprehensive capacitive performance, which may be attributed to the advantageous structural features. In a −0.85 to 0 V vs Ag/AgCl potential window, the prepared hybrid electrode delivers a high specific capacitance of 345 F g⁻¹ at a current density of 1 A g⁻¹, good cycling stability (76.4% capacity retention over 5000 consecutive cycles), and outstanding rate performance (167 F g⁻¹ at 11.4 A g⁻¹). This work may trigger the possibilities of these nanomaterials for further application in supercapacitor electrodes, specifically low-crystalline oxide/hydroxide-based electrode materials.

1. INTRODUCTION

With the decreasing availability of nonrenewable resources, there is an emerging demand for sustainable and renewable energy resources in complementing or replacing the traditional energy resources. At the forefront of renewable energy development are superior electrical performance energy storage and conversion systems that have great potential in high-power flexible electronics, chemical sensors, and electrical power applications.¹⁻⁴ A supercapacitor, also called ultracapacitor or electrochemical capacitor, has received tremendous attention as an efficient electrical energy storage device currently because of its outstanding power density (1–10 kW kg⁻¹), fast charging/discharging rates (a few seconds), and good cycle life (over 100 000 cycles).³⁻⁹ Therefore, supercapacitor not only is a promising and competitive candidate for energy storage systems but also uniquely possesses the merits of both rechargeable batteries and traditional dielectric capacitors.¹⁰ Nevertheless, insufficient energy density (~10 Wh kg⁻¹) is still the major disadvantage of supercapacitors, which could not meet the increasing energy demands for electric power applications. The key to enhancing the energy storage ability of supercapacitors is to develop advanced electrode materials because the device capacitance (C) and voltage window (V) contribute to the energy density (E = 1/2 CV²).¹¹,¹² Hence, great efforts should be devoted to developing appropriate electrode materials. Depending on the fundamental charge storage mechanisms, the supercapacitor electrode materials are of two types: (i) electrochemical double-layer capacitive (EDLC) materials (activated carbon, carbon nanotubes, graphene, and carbon fibers)¹³⁻¹⁵ and (ii) pseudocapacitive materials (transition-metal oxides/hydroxides and conductive polymers).¹⁶⁻¹⁸ Pseudocapacitive materials usually have a higher energy density owing to their fast surface/near-surface Faradic redox reactions.¹⁹,²⁰

Recently, supercapacitors have been found to achieve high energy density while maintaining their high power density. Carbon-based materials have been usually preferred as anode materials in supercapacitors thanks to their large specific surface area, outstanding electrical conductivity, and high power density; nevertheless, the attained low specific capacitance highly hinders the energy density of supercapacitors, which makes them unattractive in meeting the energy requirements of future industrial systems.²¹,²²,²³ Much research efforts have been devoted to exploring new anode materials, such as Mn/Fe/Co/Ni/Mo/V-based transition-

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metal oxides/hydroxides, to attain high specific capacitance. Among these Faradic anode materials, crystalline iron oxides/hydroxides have been commonly used as anode materials for supercapacitors owing to their large theoretical capacitance, natural abundance, and nontoxicity. Although high performance has been attained for these materials, most of them exhibit unsatisfactory stability and electrical conductivity (∼10⁻¹⁴ S/cm). A high-crystalline structure has difficulties to expand or contract, which hinder the permeation and diffusion of ions. Amorphous metal oxides are available to achieve better electrochemical activity than a crystalline phase owing to their high structural disorder and defects. To the best of our knowledge, it is still a key challenge to investigate the electrochemical performance of low-crystalline iron oxides/hydroxides, which may have potential applications in designing future supercapacitors.

Among the available alternative iron oxides/hydroxides, iron oxide hydroxide (FeOOH) have always been recognized as an appealing supercapacitor anode material because of its unique tunnel structure, providing a short electrolyte ion diffusion path. However, FeOOH displays limited specific capacitance and rate capability owing to its intrinsic weaker properties such as low specific surface area and poor electrical conductivity. Alternatively, multicomponent systems assembling FeOOH nanoparticles on a carbon matrix (graphene, active carbon, carbon black, etc.) have been proposed to enhance the capacitive performance. Based on the above discussion, we present a novel chemical method (in which the reaction proceeds in an organic solvent) to prepare low-crystalline FeOOH nanoparticles@multi-walled carbon nanotubes (FeOOH NFs@MWCNTs) hybrid nanosheets. The combined FeOOH NFs@MWCNTs heterostructures feature a low-crystalline FeOOH NF self-assembled mesoporous nanofilm tightly anchored on the MWCNTs nanosheets, presenting a large surface area and short electron transport paths, resulting in superior capacitive performance because of the rich redox reactions and enhanced electronic conductivity. Moreover, the impact of electrolytes with different pH values on the electrode electrochemical performance has also been further investigated. By optimizing the mass ratio of amorphous FeOOH NFs to MWCNTs in the composite, a remarkable specific capacitance of about 345 F g⁻¹ at 1 A g⁻¹ has been acquired for the amorphous 1FeOOH NFs@1MWCNTs hybrid nanosheets at pH 8, which delivers comparable or superior electrochemical properties to those reported for the crystalline counterpart, revealing significant improvement for exploring promising supercapacitor electrode materials.

2. RESULTS AND DISCUSSION

The amorphous FeOOH NFs@MWCNTs hybrid nanoflowers were achieved via a new facile synthesis method; the process is schematically shown in Scheme 1. The chemical reaction used in the novel synthesis process is shown below

\[
\text{FeCl}_3 + 3\text{NH}_4\text{HCO}_3 \rightarrow \text{FeOOH} + 3\text{CO}_2 + \text{H}_2\text{O} + 3\text{NH}_4\text{Cl}
\]

2.1. Characterization of Low-Crystalline FeOOH NFs@MWCNTs Hybrid Nanoflowers. Fourier transform infrared (FTIR) spectral analysis was performed in a broad band from 4000 to 400 cm⁻¹. Figure 1a illustrates the FTIR spectra of the amorphous FeOOH NFs, MWCNTs, and FeOOH NFs@MWCNTs. The absorption band located at around 3448 cm⁻¹, which was attributed to the hydroxyl groups on the samples, corresponds to the symmetric –OH bending vibrations in all of the samples. The FTIR spectrum of FeOOH NFs@MWCNTs composites exhibits characteristic bands at 1623, 1384, and 1114 cm⁻¹, which can be assigned to the oxygen-containing functional groups (C≡O, C–H, and C–O, respectively). The observed peak at 696 cm⁻¹ is assigned to the stretching vibrations of Fe–O. The representative FTIR spectrum of FeOOH NFs is the same as that of FeOOH NFs@MWCNTs, indicating that the FeOOH nanofilm is significantly anchored on the surface of MWCNTs.
The crystalline structure of the samples was identified by XRD analysis. Figure 1b shows the XRD patterns of the pristine FeOOH NFs, MWCNTs, and FeOOH NFs@MWCNTs composites. The FeOOH NFs@MWCNTs composites with different FeOOH NFs/MWCNTs mass ratios of 0.5:1, 1:1, 2:1, 3:1, and 6:1 are denoted as 0.5FeOOH NFs@1MWCNTs, 1FeOOH NFs@1MWCNTs, 2FeOOH NFs@1MWCNTs, 3FeOOH NFs@1MWCNTs, and 6FeOOH NFs@1MWCNTs, respectively. The FeOOH NF sample shows no diffraction peaks, indicating a low-crystalline structure. A peak at about 24° is obtained in the MWCNTs XRD pattern, which is assigned to the (002) reflection of MWCNTs. The FeOOH NFs@MWCNTs sample also shows the same diffraction peak, and the diffraction peak intensity is increased with the increase in the content of MWCNTs. Furthermore, all of the FeOOH NFs@MWCNTs samples show no FeOOH diffraction peaks, indicating the low-crystalline structure of FeOOH NFs in the samples.

X-ray photoelectron spectroscopy (XPS) measurements were further performed to verify the presence of the surface-bonded elements and their valence states in the 1FeOOH NFs@1MWCNTs composite. Figure 2a shows the XPS full-survey scan spectrum of the sample, revealing the presence of Fe, O, and C elements in the 1FeOOH NFs@1MWCNTs composite. The core-level spectrum of Fe 2p (Figure 2b) exhibits two characteristic binding energies at 711.6 eV (Fe 2p3/2) and 726.2 eV (Fe 2p1/2), as well as two shake-up satellite peaks (719.5 and 733.2 eV), which are highly consistent with those previously reported for amorphous FeOOH.28,30 The O 1s core-level spectrum (Figure 2c) could be deconvoluted into three chemically representative species corresponding to the Fe−O−Fe bond (530.4 eV), Fe−O−H bond (531.8 eV), and H−O−H bond (533.4 eV).11,28 Notably, the H−O−H bond is assigned to adsorbed water, which indicates that the amorphous FeOOH nanoflowers are in a hydrated form.28 The C 1s core-level spectrum is displayed in Figure 2d, which could be integrated into four main constituent peaks. The peak at a binding energy of 284.6 eV is assigned to the graphitic carbon in MWCNTs, while other three peaks correspond to the epoxy and hydroxyl (C−O, 286.2 eV), carbonyl (C=O, 287.5 eV), and oxygenated carbons of carboxyl (O−C=O, 288.4 eV), demonstrating the existence of a variety of carbon–oxygen functional groups on the surface of MWCNTs. Moreover, the formation of C−O bonds may reveal C−O−Fe, C−O−C, and C−O−H bonds in the amorphous FeOOH NFs@MWCNTs composites.28

In summary, the FTIR, XRD, and XPS results are in agreement with each other, revealing the formation of a continuous amorphous FeOOH nanoflowers on the surface of MWCNTs.

Morphological and microstructural details of the low-crystalline FeOOH NFs@MWCNTs composite (1FeOOH NFs@1MWCNTs) were identified with scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The SEM image of amorphous FeOOH NFs@MWCNTs is shown in Figure 3a, which reveals a uniformly distributed nanofilm morphology. Figure 3b shows the SEM image of the sample at high magnification, which indicates that such a microstructure is formed by the self-assembled FeOOH nanoflowers strongly attached to the MWCNTs substrate. Figure 3c presents the TEM image of FeOOH NFs@MWCNTs composites, revealing a homogeneous amorphous nanostructure. The selected area electron diffraction (SAED) pattern (inset in Figure 3c) shows a diffuse and broad diffraction halo ring, revealing the low-crystalline nature of FeOOH. The low-crystalline structure of the FeOOH NFs@MWCNTs sample could be further confirmed by high-magnification TEM (Figure 3d) and high-resolution TEM (HRTEM) images (inset in Figure 3d), which reveal that the low-crystalline FeOOH NFs are uniformly grown on the surface of MWCNTs and self-assembled to be a mesoporous nanofilm, resulting in the FeOOH NFs@MWCNTs hybrid.
nanosheets. The mesoporous structure and large surface area of the low-crystalline FeOOH nanoflowers grown on the MWCNTs surface endow the sample with short ion diffusion paths for fast ion transport and more active sites for charge storage, which are useful for improving the electrochemical performance.

2.2. Electrochemical Performance of Amorphous FeOOH NFs@MWCNTs Hybrid Nanoflowers. To study the electrochemical performance of amorphous FeOOH NFs@MWCNTs hybrid nanoflowers, cyclic voltammetry (CV) and galvanostatic charge/discharge tests were conducted in a three-electrode cell with a Pt wire counter electrode and an Ag/AgCl reference electrode in 0.5 M Na$_2$SO$_4$ aqueous electrolyte. Figure 4a exhibits the CV curves of the amorphous FeOOH NFs@MWCNTs composite electrodes with different FeOOH NFs/MWCNTs mass ratios tested at a scan rate of 10 mV s$^{-1}$ in a $-0.85$ to 0 V potential window. The CV curve of the pristine MWCNTs electrode exhibits a nearly rectangular shape, which denotes the signature of an ideal double-layer capacitance. However, the current densities of the MWCNTs electrode are much lower than those of the pseudocapacitive material electrodes, limiting the rate capability for supercapacitors. Surprisingly, the current densities are greatly increased when FeOOH NFs are introduced into MWCNTs, and the FeOOH NFs@MWCNTs composite electrodes exhibit quasi-rectangular CV curves, which is characteristic of the pseudocapacitive behavior. Figure 4b shows the specific capacitances with scan rates of FeOOH NFs@MWCNTs samples. The specific capacitance of the sample greatly

Figure 3. (a) SEM, (b) magnified SEM, (c) TEM, and (d) magnified TEM images of the 1FeOOH NFs@1MWCNTs hybrid nanoflowers. The inset in (c) is the corresponding SEAD pattern. The inset in (d) is the HRTEM for the 1FeOOH NFs@1MWCNTs composite.

Figure 4. Electrochemical performance of amorphous FeOOH NFs@MWCNTs composites: (a) CV curves of the low-crystalline FeOOH NFs@MWCNTs composite electrodes with different FeOOH NFs@MWCNTs mass ratios at a scan rate of 10 mV s$^{-1}$. (b) Specific capacitances of the MWCNTs and FeOOH NFs@MWCNTs composite electrodes as a function of the scan rate. (c) Galvanostatic charge/discharge (GCD) profiles of the amorphous FeOOH NFs@MWCNTs composite electrodes at a current density of 1 A g$^{-1}$. (d) Rate capabilities of the amorphous FeOOH NFs@MWCNTs composite electrodes as a function of current density. (e, f) Nyquist plots of the amorphous FeOOH NFs@MWCNTs composite electrodes.
The 1FeOOH NFs@1MWCNTs display a longer pseudocapacitive behavior compared with symmetric GCD curves of MWCNTs, indicating that the curves of amorphous FeOOH NFs@MWCNTs are close to ideal, with two slight potential plateaus shown in the GCD characteristic of the double-layer capacitive behavior with low to 0 V exhibit ideal symmetric triangle curves, which is analogous to the GCD curves of MWCNTs in the working voltage window of 0.85 V vs Ag/AgCl. Two slight potential plateaus are shown in the GCD characteristic of the double-layer capacitive behavior with low to 0 V exhibit ideal symmetric triangle curves, which is analogous to the GCD curves of MWCNTs in the working voltage window of 0.85 V vs Ag/AgCl.

Figure 4c shows the GCD curves of the 1FeOOH NFs@1MWCNTs composite measured at various pH values. The specific capacitance of the 1FeOOH NFs@1MWCNTs composite electrode was determined in solutions with different pH values.

Table 1. Comparison of Electrochemical Performance for Iron Oxide/Hydroxide-Based Electrodes in Neutral Aqueous Electrolytes

| iron oxide/electrode design                  | electrolyte       | voltage range                  | specific capacitance (F g⁻¹) | experimental method | ref  |
|---------------------------------------------|-------------------|--------------------------------|-----------------------------|---------------------|-----|
| FeOOH quantum dots/graphene                 | 1 M Li₂SO₄        | −0.8 to 0 V vs Ag/AgCl         | 365.0                       | CV, 10 mV s⁻¹       | 11  |
| core−shell α-FeOOH                         | 0.1 M Na₂SO₄      | 0 to 0.8 V vs Ag/AgCl          | 160.0                       | CV, 5.0 mV s⁻¹      | 17  |
| β-FeOOH composite                          | 1 M Li₃SO₄        | −0.18 to −0.93 V vs Ag/AgCl    | 116.0                       | CD, 0.5 A g⁻¹       | 32  |
| GFCNT@400Fe₂O₅                             | 2 M KOH           | −1.2 to 0 V vs Ag/AgCl         | 370.2                       | CD, 40 A g⁻¹        | 33  |
| PPy-CNT-FeOOH composites                   | 0.5 M Na₂SO₄      | −0.8 to 0.1 V vs SCE           | 121.6                       | CV, 2.0 mV s⁻¹      | 34  |
| carbon fabric, vertically aligned graphene  | 2 M KOH           | 0 to −1.1 V vs Hg/HgO          | 909.0                       | CV, 2.0 mV s⁻¹      | 35  |
| NFs@FeOOH                                  | 1 M Na₂SO₄        | 0 to −1 V vs SCE               | 159.7                       | CD, 0.5 A g⁻¹       | 36  |
| Mn−iron oxide (Mn−FeOx)                    | 1 M Na₂SO₄        | 0 to 0.8 V vs SCE              | 228.6                       | CD, 1.0 A g⁻¹       | 37  |
| FeOOH nanorod arrays/carbon tube network    | 6 M KOH           | −1.08 to 0 V vs Ag/AgCl        | 396.0                       | CD, 0.5 A g⁻¹       | 38  |
| NiNTAs@Fe₂O₃ nanoneedle                    | 1 M Na₂SO₄        | −0.8 to 0 V vs Ag/AgCl         | 418.7                       | CV, 10 mV s⁻¹       | 39  |
| amorphous FeOOH Nanoflowers@MWCNTs          | 0.5 M Na₂SO₄      | 0 to −0.85 V vs Ag/AgCl        | 345.0                       | CD, 1.0 A g⁻¹       | this work |

CV, cyclic voltammetry; CD, charge–discharge.

Figure 5. (a) GCD profiles of the 1FeOOH NFs@1MWCNTs hybrid nanosheet electrode measured at 1.25 A g⁻¹ in solutions with different pH values with a voltage window of 0.85 V. (b) Specific capacitances of the 1FeOOH NFs@1MWCNTs composite electrode with the pH value of the electrolyte. (c) Nyquist plots of the 1FeOOH NFs@1MWCNTs composite electrode in electrolytes with different pH values.

increases when FeOOH NFs are introduced into MWCNTs. When the content of FeOOH NFs increases, the specific capacitance of the electrode increases until a peak value of about 266 F g⁻¹ is achieved at 10 mV s⁻¹ for 1FeOOH NFs@1MWCNTs. Galvanostatic charge/discharge (GCD) analysis was carried out to assess the rate performance of the amorphous FeOOH NFs@MWCNTs composite. Figure 4c shows the GCD curves of the amorphous FeOOH NFs@MWCNTs with various FeOOH NFs@MWCNTs mass ratios at 1 A g⁻¹. The GCD curves of MWCNTs in the working voltage window of −0.85 to 0 V exhibit ideal symmetric triangle curves, which is characteristic of the double-layer capacitive behavior with low resistance. Two slight potential plateaus are shown in the GCD curves of amorphous FeOOH NFs@MWCNTs compared with symmetric GCD curves of MWCNTs, indicating that the pseudocapacitive behavior corresponds well with CV measurements. The 1FeOOH NFs@1MWCNTs display a longer discharge time at 1 A g⁻¹ than the other samples, which reveals a higher specific capacitance. The specific capacitance was acquired according to the discharge curves and is displayed in Figure 4d; the specific capacitance can be easily increased with the increase in the content of FeOOH NFs increases. The 1FeOOH NFs@1MWCNTs hybrid electrode exhibits a maximum specific capacitance of 350 F g⁻¹ at 1 A g⁻¹; when the mass ratio is over 1:1, the FeOOH NFs anchored on the MWCNTs surface may be overgrown, which indicates that the anchored FeOOH NFs could not completely work in the redox reaction; then, the attained specific capacitance decreases.

To provide further insights, electrochemical impedance spectroscopy (EIS) was performed on FeOOH NFs@MWCNTs composite electrodes and the homologous Nyquist plots are displayed in Figure 4e,f. For the Nyquist plot, the intercept at the Zreal axis represents equivalent series resistance (ESR) (Rₑ), a small semicircle in the high-frequency regions correlates to the charge-transfer resistance (Rct), and the slope of the low-frequency straight line corresponds to the ion diffusion resistance (Rd) in the electrolyte. The slope of the Nyquist plot of the as-prepared electrodes at low frequencies is almost vertical to Zreal, indicating a good capacitive response. This clearly indicates a trend that all resistances of the FeOOH NFs@MWCNTs composite electrodes decrease as the content of MWCNTs increases, which may be ascribed to the enlarged surface area and enhanced electron and ion transport. The EIS spectra confirmed the sample with superior electrochemical performance, as revealed by the CV and GCD measurements.

The heterostructure optimization between amorphous FeOOH NFs and MWCNTs could effectively exhibit the advantages of every single material and greatly improve the electrochemical performance. In this work, although the incorporation of MWCNTs can improve the pseudocapacitance of FeOOH NFs, the capacitance contribution of MWCNTs itself is limited, which needs a rational FeOOH NFs/MWCNTs mass ratio to acquire a high specific capacitance that can be comparable with the product of the redox process of FeOOH NFs.
capacitance of the samples and find the 1FeOOH NFs@1MWCNTs is the best in this paper.

To the best of our knowledge, the amorphous FeOOH NFs@MWCNTs hybrid nanosheet electrode developed in this work exhibits comparable or superior electrochemical performances to those reported in the literature for oxide/hydroxide-based electrodes in neutral aqueous electrolytes (Table 1).11,17,32−41

The pH value of the supporting electrolyte presents a significant influence on the 1FeOOH NFs@1MWCNTs composite electrode by affecting both the specific capacitances and impedance. Figure 5a shows GCD profiles of the electrode in 0.5 M Na₂SO₄ electrolyte with various pH values, and Figure 5b illustrates the dependencies of the specific capacitances on the electrolyte pH. The specific capacitances increase with increasing electrolyte pH value, while the specific capacitance acquires a maximum of about 320 F g⁻¹ for 1FeOOH NFs@1MWCNTs composite electrode at around pH 7. In addition, the specific capacitances shifted negatively with increasing pH, showing that ions, electrons, and protons have partly taken part in the redox reaction processes. To evaluate the electrochemical influence of the electrolyte pH value, we reported the EIS recorded in the frequency range from 1 MHz to 0.1 Hz, as depicted in Figure 5c. With the increase in the electrolyte pH value, all resistances of the composite electrodes kept decreasing. The resistance of the 1FeOOH NFs@1MWCNTs composite electrode increases with the increasing pH value of the electrolyte; however, they still exhibit excellent rate capabilities.

As a key factor to evaluate the electrochemical properties of a supercapacitor, long-term cycle stability of the low-crystalline FeOOH NFs@MWCNTs sample was studied, and the acquired results are displayed in Figure 6. For cycling performance measurement, the 1FeOOH NFs@1MWCNTs...
composite electrode was charged and discharged between −0.85 and 0 V at 1 A g⁻¹ for 1000 and 5000 cycles. Based on the GCD profiles, the acquired capacitance retentions for the 1FeOOH NFs@1MWCNTs electrode after 1000 cycles are 98.9, 85.9, 61.9, 25.4, and 20.7% in solutions with different pH values of 10, 8, 7, 6, and 4, respectively. As shown in Figure 6f, only 14.1% of the initial response was lost after 1000 cycles and 76.4% of the capacitance was retained up to 5000 cycles, indicating its long cycle life. Furthermore, the SEM images in Figure 7 show its original morphology (Figure 7a) with much more broken regions after 1000 cycles in the electrolyte with pH 4 (Figure 7b) than after 5000 cycles in the electrolyte with pH 8 (Figure 7c), which demonstrated its excellent structural stability in solutions with pH around 8.

Figure 8 displays the CV curves of the 1FeOOH NFs@1MWCNTs composite after the first, 100th, and 1000th cycles in solutions with different pH values. As illustrated in Figure 8b, the CV profile of the 1FeOOH NFs@1MWCNTs electrode after the 1000th cycle exhibits obvious redox peaks at −0.32 V for the cathodic scan and at −0.50 V for the anodic scan, which may be ascribed to the reversible valence change of Fe in FeOOH. It also displays a capacity retention of 94% after 1000 CV cycles, revealing the good cycle life of the electrode.

Sulfuric acid and sodium hydroxide were preferred to adjust the pH values of 8 was chosen for the following experiment, which is closer to that of the physical conditions. Therefore, the low-crystalline feature of the FeOOH NFs@MWCNTs composite results in excellent structural stability and superior redox reactions, revealing high performance as a supercapacitor electrode.

To exhibit the superior electrochemical performance of the amorphous 1FeOOH NFs@1MWCNTs composite electrode for electrochemical energy storage, GCD and CV measurements were conducted in a three-electrode configuration in the electrolyte with pH 8. Figure 9a shows the GCD profiles of the 1FeOOH NFs@1MWCNTs electrode measured at different current densities ranging from 0.72 to 11.43 A g⁻¹ in the voltage window between −0.85 and 0 V (vs Ag/AgCl). The GCD curves at various current densities exhibit almost symmetric and perfect symmetric triangles, demonstrating a nearly ideal capacitive behavior. In addition, GCD profiles display a small voltage drop of 0.016 V when the device begins to discharge, which is indicative of the electrode with a low equivalent series resistance (ESR). Based on the GCD profiles, the measured specific capacitances for the 1FeOOH NFs@1MWCNTs electrode are 365.54, 252.26, 203.66, 185.14, and 166.63 F g⁻¹ at 0.72, 1.43, 2.86, 5.72, and 11.43 A g⁻¹, respectively, as shown in Figure 9c. Figure 9b shows the CV profiles of the 1FeOOH NFs@1MWCNTs composite.
electrode measured at various scan rates from 10 to 100 mV s\(^{-1}\) in a −0.85 to 0 V vs Ag/AgCl voltage window. The electrode shows quasi-rectangular CV shapes at various scan rates, which is indicative of a nearly typical pseudocapacitive behavior. Additionally, the CV profiles exhibit a clear current leap near the end of −0.85 V at anodic scans. The current leaps at around −0.85 V indicate an initiation of a redox reaction, which may be attributed to the valence change of Fe. Figure 9d displays the specific capacitance of the 1FeOOH NFs@1MWCNTs electrode as a function of the scan rate. The electrode can deliver a high specific capacitance of 277.26 F g\(^{-1}\) at a scan rate of 10 mV s\(^{-1}\). With the increase of scan rate to 100 mV s\(^{-1}\), a specific capacitance of 166.73 F g\(^{-1}\) can be maintained, corresponding to 60.13% of the capacitance at 10 mV s\(^{-1}\), in agreement with its good charge storage ability.

3. CONCLUSIONS

We have successfully prepared amorphous FeOOH NFs@MWCNTs hybrid nanosheets through a facile and scalable method. The low-crystalline FeOOH NFs/MWCNTs composites possess a homogeneous heterostructure, which was constructed by a self-assembled FeOOH NF mesoporous nanofilm strongly attached to the MWCNTs substrate. Interestingly, the amorphous design of the pseudocapacitive electrode with suitable pH values of the electrolytes results in an excellent electrochemical performance for the supercapacitor electrode. By adjusting the mass ratio of amorphous FeOOH NFs and MWCNTs, the 1FeOOH NFs@1MWCNTs electrode (pH 8) displays a large specific capacitance of up to 345 F g\(^{-1}\), an outstanding rate capability, and great cycle stability. The superior electrochemical performance of the electrode may be ascribed to the following aspects: (i) the predominant capacitive contribution of the amorphous FeOOH NFs results in high specific capacitance; (ii) the mesoporous structure and high surface area of the electrode materials provide more active sites for storing energy; and (iii) the FeOOH NFs are directly anchored on conductive MWCNTs, providing fast ion/electronic transport and easy accessibility of the active materials to electrolytes. Thus, our work may provide great potential for developing low-cost environmentally benign amorphous-based supercapacitor electrode materials in electric applications.

4. EXPERIMENTAL SECTION

4.1. Materials. FeCl\(_3\)-6H\(_2\)O, NH\(_4\)HCO\(_3\), and ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd. (Ourchem Shanghai). MWCNTs were supplied by Timesnano (Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences). All chemicals employed in the present paper were analytical reagents and used as received. Carbon paper (CeTech, Taiwan) was employed as the conductive substrate for the as-synthesized materials. Deionized (DI) water with a resistivity of over 18.25 M\(\Omega\) cm at 23 °C was used throughout the experiment.

4.2. Synthesis of FeOOH NFs@MWCNTs Hybrid Nanoflowers. The amorphous FeOOH NFs@MWCNTs hybrid nanoflowers were obtained via a new facile synthesis method. In a typical preparation, 5 mmol of FeCl\(_3\)-6H\(_2\)O was added to 40 mL of ethanol and stirred for 0.5 h. Afterward, certain amounts of MWCNTs were added and dispersed by 20 min ultrasonication, which may give a uniform mixing between FeCl\(_3\) and MWCNTs in the composite. After that, 15 mmol of NH\(_4\)HCO\(_3\) was dissolved in the solution and the solution was stirred in a ventilation cabinet for 12 h. Subsequently, the obtained products were separated by centrifugation, washed several times using DI water, and dried at 80 °C in a vacuum oven for use.

4.3. Characterization. The structural characterization and phase purity of the as-prepared samples were investigated by Fourier transform infrared (FTIR, Bruker Tensor 27, Germany), X-ray diffraction (XRD, Bruker-AXS D8 Advance with monochromatized Cu Kα radiation), and X-ray photo-electron spectroscopy (XPS, Thermo Scientific Escalab 250Xi instrument). The morphological characterizations and microstructure of the as-synthesized samples were recorded by cold field emission scanning electron microscopy (SEM, HITACHI S-4800, Japan) and transmission electron microscopy (TEM, FEI, Tecnai G2 F20).

4.4. Electrochemical Measurements. The electrochemical measurements of the as-prepared samples were conducted on an electrochemical workstation (CHI 660E, Shanghai Chenhua Instruments Co.) with a standard three-electrode cell system using the as-synthesized materials on the carbon paper as the working electrode, Ag/AgCl (saturated KCl) as the reference electrode, and a Pt wire as the counter electrode. The electrochemical performances of the electrodes were assessed by cyclic voltammetry (CV), galvanostatic charge/discharge measurements (GCD), and electrochemical impedance spectroscopy (EIS) in a 0.5 M Na\(_2\)SO\(_4\) aqueous electrolyte. The EIS measurements were carried out using a sinusoidal signal over a frequency range from 0.1 to 10\(^5\) Hz, with an amplitude of 5 mV.

The specific capacitances of the electrodes were obtained from the GCD curves at various current densities using the following equation

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

where \(C_s (F g^{-1})\) is the specific capacitance, \(I\) (A) is the constant discharge current, \(\Delta t\) (s) is the discharge time, \(m\) (g) is the mass of the electroactive material, and \(\Delta V\) (V) is the discharge voltage range excluding the voltage drop.

The specific capacitances of the electrodes can also be obtained from the CV curves at different scan rates.

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Notes
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