

Article

One-Step Self-Assembly Synthesis α -Fe₂O₃ with Carbon-Coated Nanoparticles for Stabilized and Enhanced Supercapacitors Electrode

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Abstract: A cocoon-like α -Fe₂O₃ nanocomposite with a novel carbon-coated structure was synthesized via a simple one-step hydrothermal self-assembly method and employed as supercapacitor electrode material. It was observed from electrochemical measurements that the obtained α -Fe₂O₃@C electrode showed a good specific capacitance (406.9 Fg⁻¹ at 0.5 Ag⁻¹) and excellent cycling stability, with 90.7% specific capacitance retained after 2000 cycles at high current density of 10 Ag⁻¹. These impressive results, presented here, demonstrated that α -Fe₂O₃@C could be a promising alternative material for application in high energy density storage.

Keywords: one-step; self-assembly; α -Fe₂O₃; carbon coating; supercapacitors

1. Introduction

With the development of the economy, environmental pressure has been increasing, and it is very urgent to develop a new, low cost, environmentally friendly alternative energy source and energy storage system [1–4]. Supercapacitors are considered to be a promising candidate material for energy storage because of their advantages of high power density, excellent rate capacitance, long cycle life, and so on [5–7]. The supercapacitor can be classified into two categories: electric double-layer capacitors and pseudocapacitors. The charge storage capacitance in the double-layer capacitors is derived from the electrostatic forces based on the electrical double layers. While it is derived from the rapid Faraday oxidation-reduction reaction in the pseudocapacitors [8]. Electrode material is the main factor in determining the performance of supercapacitors [9]. Due to the varied oxidation states for efficient redox charge transfer and high theoretical specific capacitance, transition metal oxides have been considered to be one of the most attractive electrode materials for supercapacitors [10,11]. Hematite (Fe₂O₃), a typical transition metal oxide, has attracted a lot of attention for application in supercapacitors due to its low cost, environmental friendliness, and many other advantages [12–14]. However, Fe₂O₃ electrode material also exhibits some serious disadvantages, such as poor electrical conductivity and large volume change, impeding their commercial applications [15]. Carbon-based materials, thanks to their high electrical conductivity, excellent chemical stability, and superior mechanical properties, can be composited with Fe₂O₃ to overcome the above-mentioned shortcomings and improve electrochemical property in supercapacitors [16,17]. The coating carbon can increase the electronic conductivity of the matrix material and function as a structural buffering layer to cushion the mechanical stress caused by the large volume change during the cycling process. The coating carbon is able to improve the electrical conductivity of the matrix material and also plays as a constraint layer to buffer the cycle of large volume expansion in the charge and discharge process.

In this work, α -Fe₂O₃ with a novel carbon-coated structure nanoparticle composite was fabricated via a facile one-step self-assembly synthesis method and employed as electrode for supercapacitors. The α -Fe₂O₃@C nanoparticles exhibited excellent charge storage properties in terms of high capacitance, superior rate capability, and good cyclic stability. This unique structure is conducive to getting over the above-mentioned shortcomings of Fe₂O₃. As a result, the performance of composite materials as supercapacitors electrode could be enhanced to some extent. Therefore, the cocoon-like α -Fe₂O₃ nanoparticles with a novel carbon-coated structure have great potential for practical application in the energy storage field.

2. Experimental Section

2.1. Synthesis of α -Fe₂O₃@C Composite

All of the chemicals were analytical grade and used as received. At first, 0.06 mol Ferric chloride (FeCl₃·6H₂O) was dissolved in distilled water to form saturated FeCl₃ solution. Then, the saturated FeCl₃ solution was slowly dropped into 100 mL boiling deionized water under continuous magnetic stirring. In this process, Fe³⁺-containing solution was hydrolyzed to Fe(OH)₃ colloid with negative charge and presented evident Tyndall phenomenon. After several minutes, 10 mL Poly dimethyl diallyl ammonium chloride ((C₈H₁₆ClN)_n, Mw < 100,000, 35 wt %, Aladdin) (PDDA) solution was gradually added into the homogeneous colloid solution with the assist of magnetic stirring continuously for 3 h. The mixture of the two solutions was then sealed in Teflon-lined stainless steel autoclave at 180 °C for 12 h and cooled down to room temperature. PDDA solution is a type of polycation electrolytes with positive charge. Negatively charged Fe(OH)₃ colloidal precursors and positively charged organics were self-assembled under the action of Vander Waals molecular force in the hydrothermally reaction procedure. In the boiling water, Fe³⁺ solution was hydrolyzed into Fe(OH)₃ colloid. Then, the colloidal particles were decomposed into Fe₂O₃ in the subsequent hydrothermal reaction. The relevant chemical reactions are shown as follows:



The resulting suspension solution was centrifuged, and then the precipitate was washed with distilled water and anhydrous ethanol. Finally, the collected precipitate was dried at 80 °C in air followed by carbonization at 350 °C for 2 h under highly pure nitrogen (N₂) to obtain α -Fe₂O₃@C composite powder samples.

2.2. Materials Characterization

The structure of the material was examined by X-ray diffraction (XRD, D8 Advance, Bruker AXS, Karlsruhe, Germany) with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) in the range from 5–80°. The X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermo Fisher Scientific, Waltham, MA, USA) was conducted with X-ray instrument with an Al K $\alpha = 300.0 \text{ eV}$ excitation source.

The morphology of the active as-prepared sample was examined by field emission scanning electron microscope (FESEM, Zeiss Ultra Plus, ZEISS, Oberkochen, Germany) and transmission electron microscopy (TEM, JEM 2100F, JEOL, Tokyo, Japan). The element mapping images were obtained on an energy dispersive X-ray spectrometry (EDS, Oxford Instruments, Abingdon, UK). Thermogravimetric analysis-Differential scanning calorimetry (TG-DSC, STA449F3, NETZSCH, Selb, Germany) was conducted in air from room temperature to 1000 °C with heating rate of 10 °C/min.

Raman spectra (INVIA, Renishaw Co. Ltd., Gloucestershire, UK) were analyzed with 632.5 nm argon ion laser from 100 to 1800 cm^{−1}. Fourier transform infra-red (FTIR) spectra (Nexus, Thermo Nicolet, Madison, WI, USA) were conducted in the spectral ranges of 400–4000 cm^{−1}. The specific surface areas of samples were recorded using nitrogen adsorption-desorption isotherms via

Brunauer-Emmett-Teller (BET, ASAP 2020M, Micromeritics Instrument, Norcross, GA, USA) analysis at 77 K.

2.3. Electrochemical Measurements

All electrochemical measurements were performed on a CHI660E electrochemical workstation in a typical three-electrode system, with platinum foil and Hg/HgO as the counter electrode and reference electrode, respectively, and the electrolyte was 6 M KOH aqueous solution. The electrochemical impedance spectroscopy (EIS) measurements were carried out on an electrochemical workstation (CHI660E, Chenhua Co. Ltd., Shanghai, China), and the frequency of AC impedance ranges from 0.01–106 Hz with 5 mV amplitude.

The working electrode consisted of as-prepared α -Fe₂O₃@C sample, acetylene black and polytetrafluoroethylene (PTFE) solution in a weight ratio of 70:20:10. The mixture was ground into a mash and then pressed into a sheet by a double roller press and punched into small disks with diameter of 1.0 cm. The disks were wrapped in nickel foam by rolling to form a sandwich structure and used as the working electrode. Each working electrode contained about 2.5 mg α -Fe₂O₃@C active material. The preparation process of sandwich structures working electrode was schematic illustrated in Figure 1. Compared with electrode prepared via conventional method in which the slurry was directly coated on the nickel foam, the electrode with the sandwich structure prepared by this method was harder to fall off.

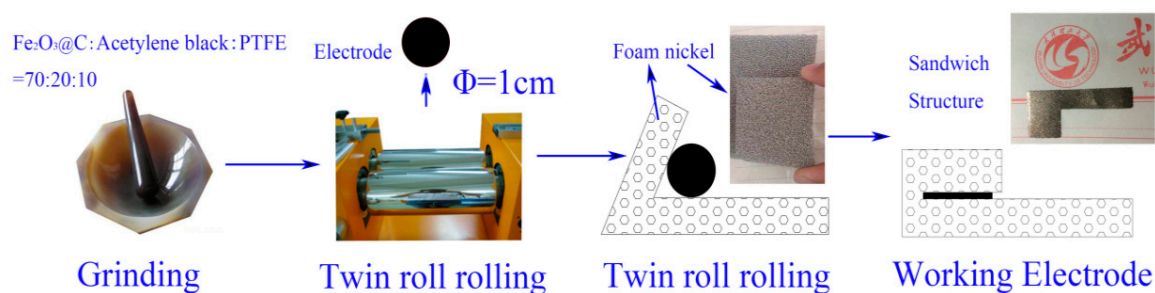


Figure 1. Schematic illustration of preparation of sandwich structure working electrode.

3. Results and Discussion

XRD patterns of α -Fe₂O₃@C samples before and after calcination in N₂ are shown in Figure 2. After calcination, the crystal phase of the samples almost remained unchanged. All obvious diffraction peaks were matched well with the standard α -Fe₂O₃ card (JCPDS No. 33-0664). No impurities phases have been detected and the sample is hexagonal phase α -Fe₂O₃ crystalline structure. No carbon phase peaks have been detected, which indicates that the coated carbon is amorphous. The carbonization temperature under 350 °C is not enough to lead to organic matter graphitization, so the coated carbon layer in this case is in the form of amorphous condition.

As shown in Figure 3a, six Raman scattering peaks are observed at 200–600 cm^{−1} referring to typical hematite [18], which indicates that the iron oxide precursor has been successfully synthesized by a one-step hydrothermal self-assembly process. The D band is associated with disorder carbon, resulting from various types of defects, while G band is associated with the E_{2g} mode of the crystalline graphite [3]. The intensity ratio of D peak and G peak is used to characterize the degree of graphitization of carbon. After calcination, the relative intensity of D peak and G peak is enhanced due to carbonation of organic matter during the calcination process under the high purity N₂. The peaks appeared at ~1320 cm^{−1} and ~1580 cm^{−1} are ascribed to the disordered (D) and graphitic (G) band, respectively. Compared with D peak, the intensity of G peak is very weak, indicating that the coated carbon is mainly in an amorphous state. This result is consistent with the XRD analysis of Figure 2.

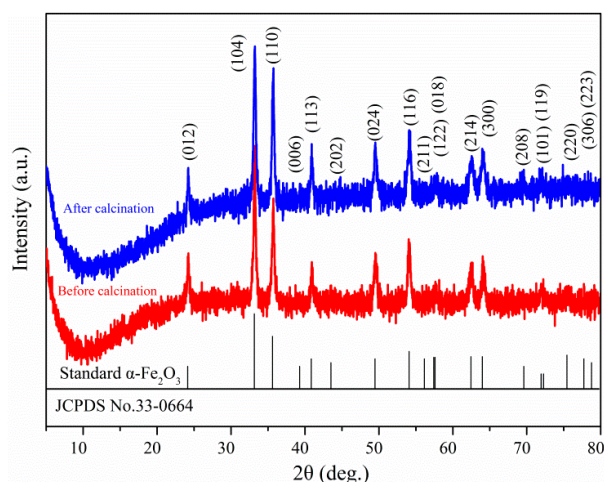


Figure 2. X-ray diffraction (XRD) patterns of α -Fe₂O₃@C nanoparticle composite before and after calcination.

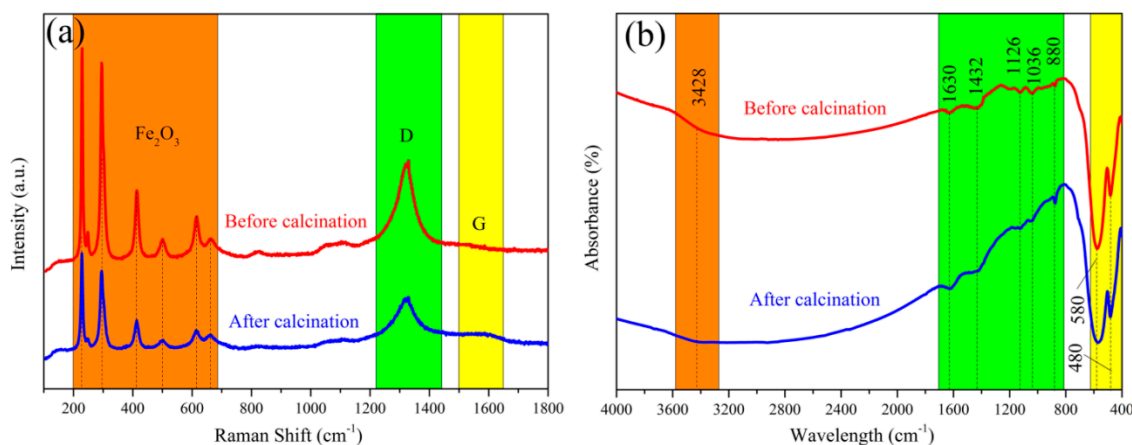


Figure 3. (a) Raman spectrums and (b) FTIR of α -Fe₂O₃@C nanoparticle composite before and after calcination.

From Figure 3b, there is a broad absorption peak located at in $\sim 3430\text{ cm}^{-1}$ corresponding to the stretching vibration of hydroxyl ($-\text{OH}$) mode of crystallized water or physically adsorbed water on the material surface. The intensity of this peak decreases after calcination, which result from the loss of some crystalline water caused by the calcination process. The absorption peaks appearing at the ~ 480 and $\sim 580\text{ cm}^{-1}$ correspond to the Fe–O vibrational mode of typical hematite [19,20]. In the fingerprint peak part ($\sim 800\text{--}1700\text{ cm}^{-1}$), the absorption peaks located at 1126, 1432, and 1630 cm^{-1} are attributed to the C–C, C–O, and C=C groups of carbon, respectively [21]. The peaks at 1036 cm^{-1} and 880 cm^{-1} are attributed to the characteristic breathing mode of residual organic matter [22]. After calcination, the relative absorption peak intensity becomes larger. All the above-mentioned absorption bands are matched well with spectroscopic characterizations of typical hematite and amorphous carbon structures, indicating the successful formation of α -Fe₂O₃@C composite via one-step self-assembly method. This result is in agreement with the XRD and Raman analysis results presented above.

As shown in Figure 4, the α -Fe₂O₃@C sample presents uniform cocoon-like oval spheres with small particle size of $\sim 500\text{ nm}$ in diameter and $\sim 1\text{ }\mu\text{m}$ in length. The particles are distributed evenly without agglomeration. It is worth noting that α -Fe₂O₃@C sample clearly reveals its hollow pore structure on the surface (Figure 4c), which can effectively buffer the volume change of Fe₂O₃. This pore

structure provides a high specific surface and more active sites and increases the electronic conduction for energy storage [23].

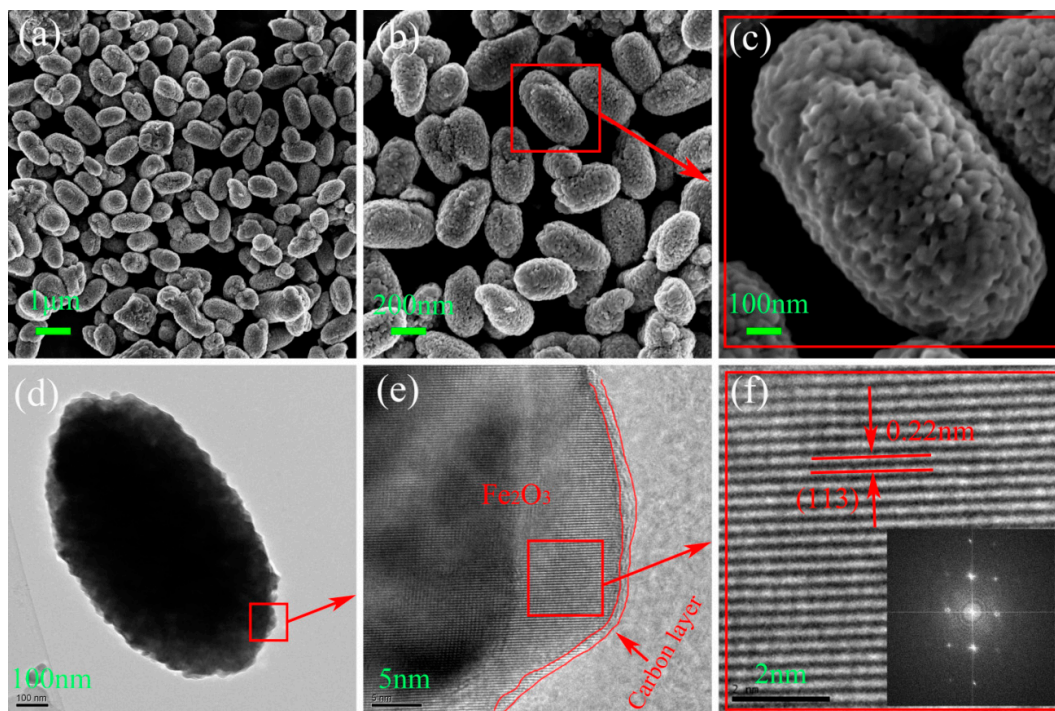


Figure 4. (a–c) field scanning electron microscopy (FESEM) and (d–f) transmission electron microscopy (TEM) images of α -Fe₂O₃@C nanoparticle composite. The insert is the selected area electron diffraction (SAED) image.

TEM was employed to further investigate the microstructures of the α -Fe₂O₃@C sample. As shown in Figure 4d, there is a light colored coating layer in the edge of the cocoon-like oval ball. With clear lattice fringes, the α -Fe₂O₃@C samples present typical crystalline structure of α -Fe₂O₃. While, no lattice fringes are observed in the coating layer of the edge of α -Fe₂O₃, indicating that the coating layer is amorphous carbon. The uniform and continuous coating layer has a thickness of a few nanometers (Figure 4e).

The HRTEM images (Figure 4f) display a set of parallel fringes with the space separation of 0.22 nm, corresponding to the (113) plane of crystalline α -Fe₂O₃ (JCPDS No. 33-0664). The selected area electron diffraction (SAED) image (the insert in Figure 4f) indicates that the α -Fe₂O₃@C sample has a perfect crystal structure. In the α -Fe₂O₃@C nanocomposites, the carbon coating layer not only serves as a conductive network but also prevents iron oxide particles from volume variation, which is crucial in improving the performance of Fe₂O₃ electrode [24].

The EDS element mapping of the α -Fe₂O₃@C sample was also studied. In order to avoid carbon pollution, the powder samples were ultrasonically dispersed in an ethanol solution, dropping on aluminum foil for test. The Fe, O and C elements are found and distributed evenly in the surface of cocoon-like nanospheres (Figure 5b). The signal of C comes from the carbon-coated layers formed during the calcination process with the organic material PDDA, demonstrating that carbon is successfully coated on the Fe₂O₃ surfaces. As shown in Figure 5f, the Al peak is derived from aluminum foil, and the carbon weight fraction in α -Fe₂O₃@C sample was about 4.09%. The quality ratio of iron and oxygen element is 66.33% and 29.58%, respectively, agreeing well with the composition ratio of iron oxide.

In order to determine the weight fraction of carbon coated in the α -Fe₂O₃@C sample more accurately, TG-DSC analysis was conducted. As shown in Figure S1, the carbon quality content in

α -Fe₂O₃@C sample was about 3.91%, which was almost the same as the result of EDS elemental analysis in Figure 5f. These analyses indicate that carbon has been ideally grown on the surface of Fe₂O₃ and the amount of the coating carbon is about 4.0%.

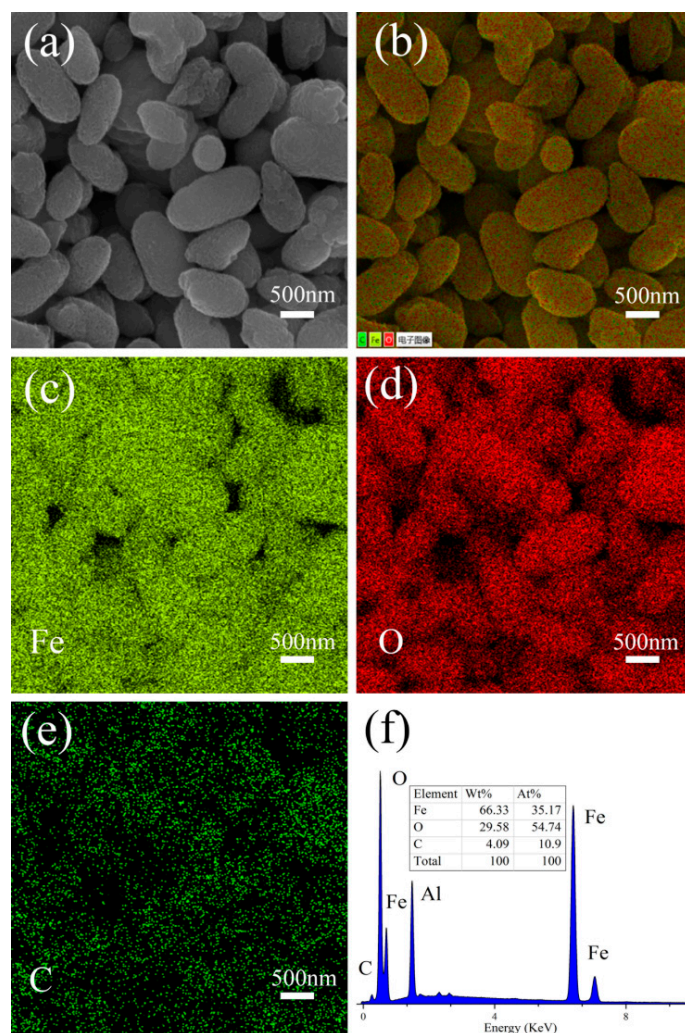


Figure 5. Energy dispersive X-ray spectrometry (EDS) element mapping of α -Fe₂O₃@C nanoparticle composite. (a) The original FESEM images; (b) the total element mapping; (c) the Fe K α 1 mapping; (d) the O K α 1 mapping; (e) the C K α 1 mapping; (f) the EDS spectra of α -Fe₂O₃@C nanoparticle.

The XPS analysis was further employed to determine the chemical compositions and bonding conditions of α -Fe₂O₃@C nanoparticle composite. One can observe clearly the peaks of Fe2p at ~720 eV, C1s peak at 285.0 eV and O1s peak at 530.5 eV from the full-range XPS survey (Figure 6a). The high-resolution spectra of Fe2p, O1s and C1s were plotted in Figure 6b–d, respectively. The Fe2p_{1/2} and Fe2p_{3/2} peaks were observed at 710.8 eV and 724.4 eV, respectively, with the binding energy difference is 13.6 eV. There are two typical satellite peaks (719.3 and 732.3 eV) near the main peak, indicating that iron exists as a trivalent form of Fe³⁺ [25–27].

In Figure 6c, the O1s binding energy is 530.0 eV, corresponding to the typical binding energy of Fe–O bonding, while the peak at 531.3 eV is assigned to C–O, C=O, and O=C–O bonds [28,29]. In Figure 6d, C1s peak can be best fit with four components which is matched well with C sp² (C=C, 284.1 eV), C sp³ (C–C, 284.6 eV), C–O (285.7 eV), and C=O (288.5 eV) [30]. The C sp² and C sp³ peaks represent graphitized carbon and amorphous carbon, respectively [31]. The C sp³ peak content is 77.9%, indicating that the coating carbon on α -Fe₂O₃ surface mainly exists in the form of amorphous carbon.

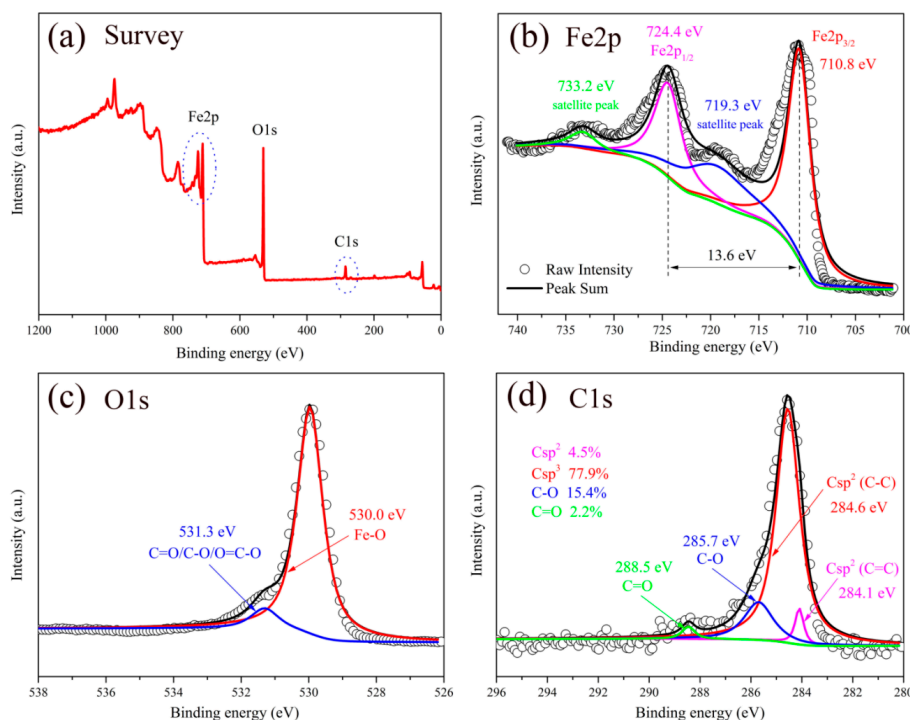


Figure 6. X-ray photoelectron spectroscopy (XPS) spectrum of α -Fe₂O₃@C nanoparticle composite. (a) The full-range XPS survey and the high-resolution spectrum of (b) Fe2p, (c) O1s and (d) C1s.

The specific surface area of the nanoparticles samples was calculated by the BET method with Nitrogen adsorption-desorption isotherms. The Nitrogen adsorption-desorption isotherms of α -Fe₂O₃@C composite exhibit type IV characteristics, which indicate the presence of mesoporous in the sample [32]. As shown in Figure 7, the corresponding pore size distributions are estimated by the Barrett-Joyner-Halenda (BJH) method. The average pore diameters and pore volume are estimated to be ~17 nm and ~0.0001 cm³ g^{−1} nm^{−1}, respectively, indicating that the α -Fe₂O₃@C composite has a mesoporous structure. During the carbonization process of organic matter PDDA, the organic matter can be used as pore-forming agent to increase the pore size by the generation of bubbles [33]. The BET specific area of α -Fe₂O₃@C sample is ~4.66 m² g^{−1}. A large surface area can increase the contact area of electrolyte/electrode and reduce the current density per unit surface area during the electrode reaction process [34]. Moreover, the large specific area and pore diameter can promote the diffusion and mass transfer of the electrolyte. The internal pores of the electrode material can be used as active sites for charge storage, improving the capacitance properties of the electrode material [35,36].

To evaluate the properties of the α -Fe₂O₃@C sample as supercapacitors electrodes, we performed CV (−1.05–(−0.3 V)) and galvanostatic charge-discharge (−1.0–(−0.3 V)) measurements. According to the Randles Sevcik equation [37,38], if taking the peak current values of CV curves and plotting logarithm of peak current values versus logarithm of scan rate, the slope is ~0.75, indicating that the α -Fe₂O₃@C mainly shows double-layer capacitance and pseudocapacitive behavior. Therefore, this system could be described as a supercapacitor.

The CV curves of α -Fe₂O₃@C exhibit a pair of typical redox peak, indicating good faradaic reactions at the electrode surface with the pseudocapacitance charging mechanism. The anodic oxidation peak corresponds to the oxidation of Fe²⁺ to Fe³⁺ and the cathodic peak corresponds to the reduction of Fe³⁺ to Fe²⁺ [39,40]. With the scanning rate increasing, the potential difference between the anodic and the cathodic peak in the CV curve does not change too much. This indicates a good electrochemical reversibility of α -Fe₂O₃@C electrode material, which results from the kinetics of the interfacial faradaic redox reactions as well as the rapid electron transport [41].

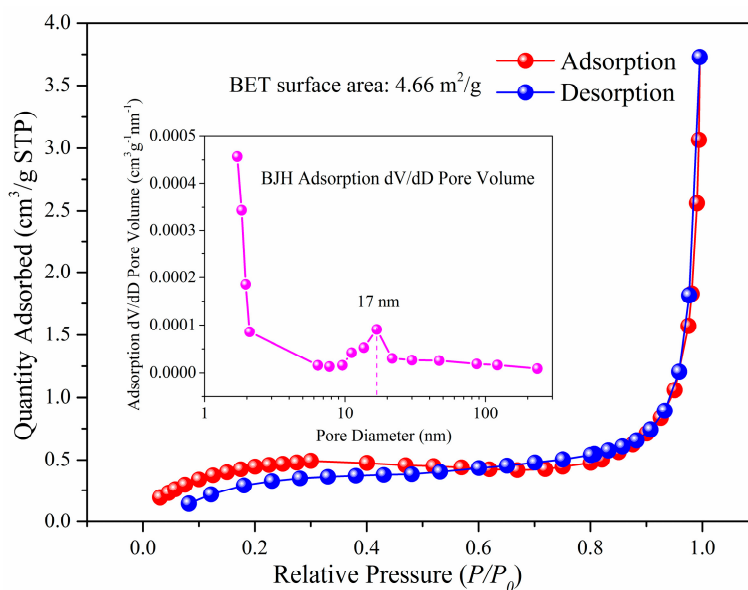


Figure 7. N_2 adsorption-desorption isotherm of $\alpha\text{-Fe}_2\text{O}_3\text{@C}$ nanoparticle composite. The insert is BJH pore size distribution.

As can be seen from Figure 8b, the discharge branch consists of two parts. The voltage drops quickly at the beginning of the discharge curve and is then followed by a slow decay, which is related to the capacitance and internal resistance of the electrode [42]. For the $\text{Fe}_2\text{O}_3\text{@C}$ electrode, there is a combination of Faraday capacitance and electric double layer capacitance, with a Faraday charge transfer and associated with electric double-layer charge transfer, resulting in longer discharge duration.

The mass specific capacitances (C) were calculated by equation $C = (I \times \Delta t) / (m \times \Delta V)$ where I is the constant discharge current (A), Δt is the discharging time (s), m is the mass of active electrode material $\alpha\text{-Fe}_2\text{O}_3\text{@C}$ (g), and ΔV is the voltage drop upon discharging (V). The value of capacitances are 406.9, 354.4, 304.9, 272.6, 224.3, and 162.8 Fg^{-1} at current densities of 0.5, 1.0, 2.0, 5.0, 10.0, and 20.0 Ag^{-1} , respectively.

The cycling life is an important indicator of the performance of supercapacitors, therefore the cycling stability of $\alpha\text{-Fe}_2\text{O}_3\text{@C}$ was investigated by repeating the charge-discharge tests at a high current density of 10 Ag^{-1} for 2000 cycles. It is found that after 2000 cycles, the specific capacitance of $\alpha\text{-Fe}_2\text{O}_3\text{@C}$ electrode material is 191.3 Fg^{-1} by remaining 90.7% of its initial specific capacitance (210.8 Fg^{-1}). In addition, the last 10 charge-discharge cycles at a current density of 10 Ag^{-1} demonstrate a stable and reversible characteristic without obvious downward trend. This may be due to the sandwich structure of $\alpha\text{-Fe}_2\text{O}_3\text{@C}$ electrode. The electrode material is not easy to fall off, and both sides of the Ni foam current collector are easy to charge conduction.

According to the literature [43], nickel foam also has a certain specific capacitance. In order to avoid the interference of Ni foam, CV (-1.0 –(-0.3 V)) and galvanostatic charge-discharges (-1.0 –(-0.3 V)) were performed in a three-electrode cell equipped with a piece of Ni foam ($1 \text{ cm} \times 1 \text{ cm}$) as working electrode (without any active electrode material loaded on this Ni foam). The results were shown in Figure S2. The values of capacitances of blank Ni foam are 1.17, 0.94, and 0.81 Fg^{-1} at current densities of 0.1, 0.2, and 0.5 Ag^{-1} , respectively. The specific capacitance of the blank Ni foam is rather small, indicating that the excellent specific capacitance performance is mainly derived from the $\alpha\text{-Fe}_2\text{O}_3\text{@C}$ electrode material.

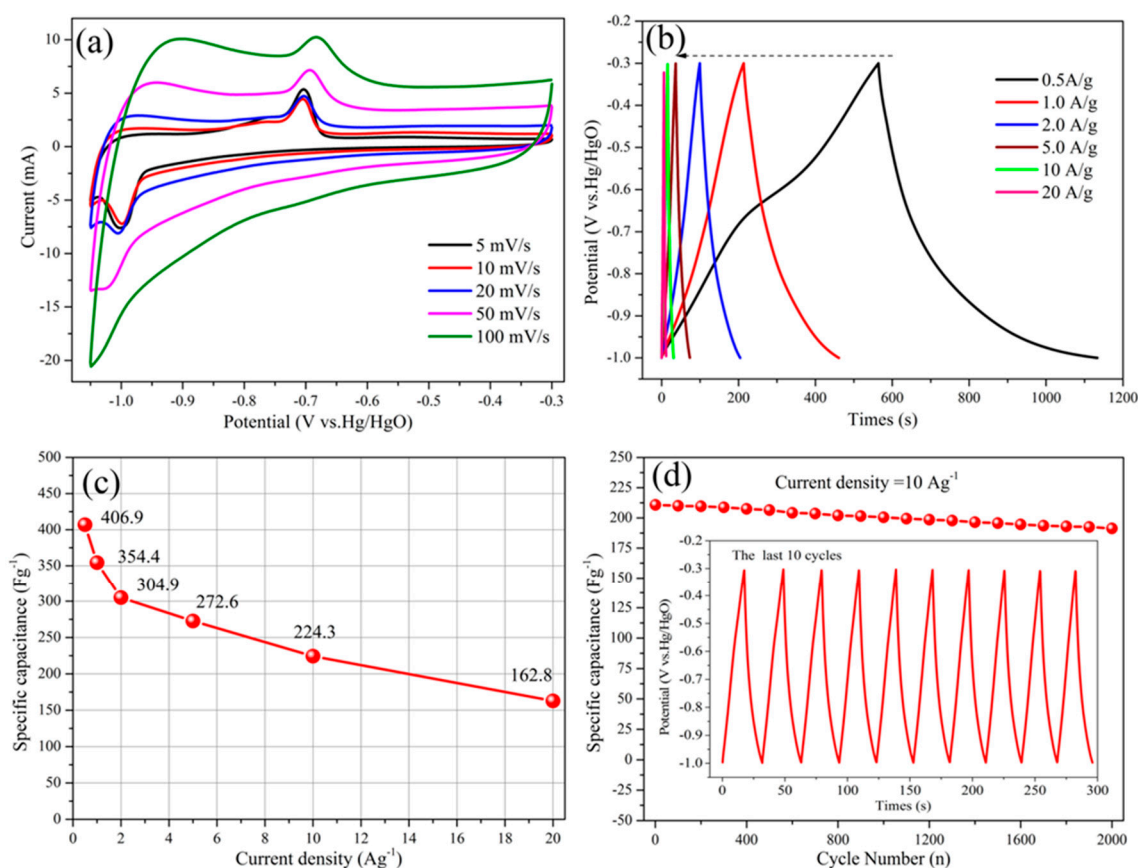


Figure 8. (a) CV curves of $\alpha\text{-Fe}_2\text{O}_3\text{@C}$ electrodes at different scan rate; (b) charge-discharge curves of $\alpha\text{-Fe}_2\text{O}_3\text{@C}$ electrodes at different current density; (c) the specific capacitance of $\alpha\text{-Fe}_2\text{O}_3\text{@C}$ electrodes at different current densities; (d) cycling stability of $\alpha\text{-Fe}_2\text{O}_3\text{@C}$ electrodes at the current density of 10 A g^{-1} , the insert is the last 10 charge-discharge cycles.

Table 1 summarizes some results of Fe_2O_3 -based material used as supercapacitor electrodes in recent reports. It is also noted that our result in this paper exhibits higher specific capacitance than those reported in the literature at the corresponding current density. This excellent capacitive performance may be due to the fact that this unique carbon coating structure maintains the rapid transmission of electrolyte ions and electrons across the electrode, which efficiently utilizes pseudo-layers and double-layer capacitance to effectively improve the electrochemical performance of Fe_2O_3 electrode material [44,45]. This outstanding capacitance performance enables the $\alpha\text{-Fe}_2\text{O}_3\text{@C}$ nanocomposites to be promising electrode materials for next-generation energy storage and conversion devices.

The EIS behaviors of $\text{Fe}_2\text{O}_3\text{@C}$ sandwich structure working electrode were further investigated (Figure S3). The Nyquist plots in the high frequency region show low internal resistance with a small equivalent series resistance ($<0.1 \Omega$, the inset of Figure S3), due to the carbon coating improves the conductivity of the Fe_2O_3 material. In the low frequency region, the Nyquist plots exhibit a straight line, representing the diffusion limited electron transfer process of $\text{Fe}_2\text{O}_3\text{@C}$ electrode.

Table 1. Comparison of Fe₂O₃-based electrode reported in recent literature using three-electrode system for supercapacitor applications.

Fe ₂ O ₃ -Based Electrode	Synthesis Method	Electrolyte	Potential Range (V)	Specific Capacitance (Fg ⁻¹)/(Ag ⁻¹)	Reference (year)
Fe ₂ O ₃ -graphene	solution-based hydrothermal	2 M KOH	−0.85–0	151.8/1.0 94/16	[46] (2012)
Porous α-Fe ₂ O ₃	Sol-gel route	0.5 M Na ₂ SO ₄	−0.8–0	193/1.0 90/5.0	[47] (2013)
g-C ₃ N ₄ /α-Fe ₂ O ₃	ionic liquid assisted solvothermal	2.5 M Li ₂ SO ₄	−1–0	260/0.5 87/5.0	[20] (2014)
N-doped graphene/Fe ₂ O ₃	hydrothermal	1 M Na ₂ SO ₄	−0.85–(−0.1)	260.1/2.0 145.1/5.0	[48] (2014)
N-rGO/Fe ₂ O ₃	hydrothermal	1 M KOH	−1~0	268.4/2.0 137/5.0	[17] (2015)
α-Fe ₂ O ₃	Template method	6 M KOH	−1.2–(−0.5)	330/0.5	[49] (2016)
Fe ₂ O ₃ NDs@N-graphene	one-pot solvothermal	2 M KOH	−1.0–0	274/1.0 201/5.0	[50] (2016)
Fe ₂ O ₃ @MnO ₂	two-step method	3 M KOH	−0.4–0.4	289.9/1.0 118.3/5.0	[40] (2017)
Fe ₂ O ₃ @C-rGO	hydrothermal	1 M Na ₂ SO ₄	−0.5–0.5	211.4/0.5 177.2/20	[51] (2017)
α-Fe ₂ O ₃ NTs/rGO	hydrothermal	1 M Na ₂ SO ₄	−0.8–0	262/1.0 196.3/5.0	[52] (2017)
Fe ₂ O ₃ @C	hydrothermal self-assembly	6 M KOH	−1.0–(−0.3)	304.9/2.0 162.8/20	This work

As shown in Figure S4a,b, the nickel foam has a homogeneous porous structure, which facilitates the separation of the electrolyte and electrons. The pore size is about 200 nm. Before the cycling, the Fe₂O₃@C nanospheres, acetylene black and polytetrafluoroethylene (PTFE) are evenly distributed. The linear object is the binder (PTFE). After the cycling, the Fe₂O₃@C nanospheres morphology remain intact, with no significant expansion and rupture, which is due to the protective effect of carbon coating. Generally, the structure of Fe₂O₃ particles will break and collapse during the cycling process. The morphology and structure of Fe₂O₃@C sample were almost unchanged and still maintained the cocoon-shaped oval spherical structure. This further illustrated that the carbon coating can effectively buffer the volume expansion of Fe₂O₃ material to maintain structural stability and improve electrical properties [53].

4. Conclusions

In conclusion, we have successfully synthesized cocoon-like α-Fe₂O₃@C nanocomposites with a novel carbon-coated core-shell structure via a simple one-step hydrothermal self-assembly method and employed it as supercapacitor electrode material. The coating carbon layer improves the conductivity of α-Fe₂O₃ and also buffers its volume change during cycling. The porous structure of α-Fe₂O₃@C provides more active sites for charge storage, which effectively enhance the specific capacitance, cycling stability, and rate performance of α-Fe₂O₃. This one-step synthesis method is simple and efficient. It is suited for the large-scale production of other carbon-coated metal oxide materials. This cocoon-like α-Fe₂O₃ nanoparticle with a novel carbon-coated structure has potential for energy storage applications.

Supplementary Materials: Supplementary materials can be found at www.mdpi.com/1996-1073/10/8/1296/s1.

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References

1. Wang, G.; Zhang, L.; Zhang, J. A review of electrode materials for electrochemical supercapacitors. *Chem. Soc. Rev.* **2012**, *41*, 797–828. [[CrossRef](#)] [[PubMed](#)]
2. Nithya, V.D.; Arul, N.S. Review on α -Fe₂O₃ based negative electrode for high performance supercapacitors. *J. Power Sources* **2016**, *327*, 297–318. [[CrossRef](#)]
3. Xiong, G.; Meng, C.; Reifengerger, R.G.; Irazoqui, P.P.; Fisher, T.S. Graphitic Petal Electrodes for All-Solid-State Flexible Supercapacitors. *Adv. Energy Mater.* **2013**, *4*, 1300515. [[CrossRef](#)]
4. Xiang, D.; Yin, L.; Wang, C.; Zhang, L. High electrochemical performance of RuO₂-Fe₂O₃ nanoparticles embedded ordered mesoporous carbon as a supercapacitor electrode material. *Energy* **2016**, *106*, 103–111. [[CrossRef](#)]
5. Peng, X.; Peng, L.; Wu, C.; Xie, Y. Two dimensional nanomaterials for flexible supercapacitors. *Chem. Soc. Rev.* **2014**, *43*, 3303–3323. [[CrossRef](#)] [[PubMed](#)]
6. Shivakumara, S.; Penki, T.R.; Munichandraiah, N. High specific surface area α -Fe₂O₃ nanostructures as high performance electrode material for supercapacitors. *Mater. Lett.* **2014**, *131*, 100–103. [[CrossRef](#)]
7. Lin, F.; Li, X.; Zhao, Y.; Yang, Z. Control Strategies with Dynamic Threshold Adjustment for Supercapacitor Energy Storage System Considering the Train and Substation Characteristics in Urban Rail Transit. *Energies* **2016**, *9*, 257. [[CrossRef](#)]
8. Baughman, R.H.; Zakhidov, A.A.; De Heer, W.A. Carbon Nanotubes—The Route Toward Applications. *Science* **2002**, *297*, 787–792. [[CrossRef](#)] [[PubMed](#)]
9. Wu, Z.S.; Zhou, G.; Yin, L.C.; Ren, W.; Li, F.; Cheng, H.-M. Graphene/metal oxide composite electrode materials for energy storage. *Nano Energy* **2012**, *1*, 107–131. [[CrossRef](#)]
10. Nan, H.; Yu, L.; Ma, W.; Geng, B.; Zhang, X. Flexible superior electrode architectures based on three-dimensional porous spinous α -Fe₂O₃ with a high performance as a supercapacitor. *Dalton Trans.* **2015**, *44*, 9581–9587. [[CrossRef](#)] [[PubMed](#)]
11. Zheng, X.; Han, Z.; Chai, F.; Qu, F.; Xia, H.; Wu, X. Flexible heterostructured supercapacitor electrodes based on α -Fe₂O₃ nanosheets with excellent electrochemical performances. *Dalton Trans.* **2016**, *45*, 12862–12870. [[CrossRef](#)] [[PubMed](#)]
12. Wang, Z.; Liu, C.J. Preparation and application of iron oxide/graphene based composites for electrochemical energy storage and energy conversion devices: Current status and perspective. *Nano Energy* **2015**, *11*, 277–293. [[CrossRef](#)]
13. Wang, L.; Yang, H.; Liu, X.; Zeng, R.; Li, M.; Huang, Y.; Hu, X. Constructing Hierarchical Tectorum-like α -Fe₂O₃/PPy Nanoarrays on Carbon Cloth for Solid-State Asymmetric Supercapacitors. *Angew. Chem. Int. Ed.* **2017**, *129*, 1125–1130. [[CrossRef](#)]
14. Yang, X.; Sun, H.; Zhang, L.; Zhao, L.; Lian, J.; Jiang, Q. High Efficient Photo-Fenton Catalyst of α -Fe₂O₃/MoS₂ Hierarchical Nanoheterostructures: Reutilization for Supercapacitors. *Sci. Rep.* **2016**, *6*, 31591. [[CrossRef](#)] [[PubMed](#)]
15. Liu, S.; Sun, S.; You, X. Inorganic nanostructured materials for high performance electrochemical supercapacitors. *Nanoscale* **2014**, *6*, 2037–2045. [[CrossRef](#)] [[PubMed](#)]
16. Gao, Y.; Wu, D.; Wang, T.; Jia, D.; Xia, W.; Lv, Y.; Cao, Y.; Tan, Y.; Liu, P. One-step solvothermal synthesis of quasi-hexagonal Fe₂O₃ nanoplates/graphene composite as high performance electrode material for supercapacitor. *Electrochim. Acta* **2016**, *191*, 275–283. [[CrossRef](#)]
17. Liu, H.D.; Zhang, J.L.; Xu, D.D.; Huang, L.H.; Tan, S.Z.; Mai, W.J. Easy one-step hydrothermal synthesis of nitrogen-doped reduced graphene oxide/iron oxide hybrid as efficient supercapacitor material. *J. Solid State Electrochem.* **2014**, *19*, 135–144. [[CrossRef](#)]
18. Yu, W.; Zhang, L.; Hou, P.; Li, F.; Liu, C.; Cheng, H. High Reversible Lithium Storage Capacity and Structural Changes of Fe₂O₃ Nanoparticles Confined inside Carbon Nanotubes. *Adv. Energy Mater.* **2016**, *6*, 1501755. [[CrossRef](#)]

19. Wang, S.; Hu, L.; Hu, Y.; Jiao, S. Conductive polyaniline capped Fe_2O_3 composite anode for high rate lithium ion batteries. *Mater. Chem. Phys.* **2014**, *146*, 289–294. [[CrossRef](#)]
20. Xu, L.; Xia, J.; Xu, H.; Yin, S.; Wang, K.; Huang, L.; Wang, L.; Li, H. Reactable ionic liquid assisted solvothermal synthesis of graphite-like C_3N_4 hybridized $\alpha\text{-Fe}_2\text{O}_3$ hollow microspheres with enhanced supercapacitive performance. *J. Power Sources* **2014**, *245*, 866–874. [[CrossRef](#)]
21. Shou, Q.; Cheng, J.; Zhang, L.; Nelson, B.J.; Zhang, X. Synthesis and characterization of a nanocomposite of goethite nanorods and reduced graphene oxide for electrochemical capacitors. *J. Solid State Chem.* **2012**, *185*, 191–197. [[CrossRef](#)]
22. Xiang, Q.; Yu, J.; Jaroniec, M. Preparation and Enhanced Visible-Light Photocatalytic H_2 -Production Activity of Graphene/ C_3N_4 Composites. *J. Phys. Chem. C* **2011**, *115*, 7355–7363. [[CrossRef](#)]
23. Meher, S.K.; Justin, P.; Rao, G.R. Microwave-mediated synthesis for improved morphology and pseudocapacitance performance of nickel oxide. *ACS Appl. Mater. Interfaces* **2011**, *3*, 2063–2073. [[CrossRef](#)] [[PubMed](#)]
24. Dong, X.; Li, L.; Zhao, C.; Liu, H.-K.; Guo, Z. Controllable synthesis of RGO/ Fe_xO_y nanocomposites as high-performance anode materials for lithium ion batteries. *J. Mater. Chem. A* **2014**, *2*, 9844–9850. [[CrossRef](#)]
25. Cao, K.; Jiao, L.; Liu, H.; Liu, Y.; Wang, Y.; Guo, Z.; Yuan, H. 3D Hierarchical Porous $\alpha\text{-Fe}_2\text{O}_3$ Nanosheets for High-Performance Lithium-Ion Batteries. *Adv. Energy Mater.* **2014**, *5*, 1401421. [[CrossRef](#)]
26. Sun, Z.; Yuan, H.; Liu, Z.; Han, B.; Zhang, X. A Highly Efficient Chemical Sensor Material for H_2S : $\alpha\text{-Fe}_2\text{O}_3$ Nanotubes Fabricated Using Carbon Nanotube Templates. *Adv. Mater.* **2005**, *17*, 2993–2997. [[CrossRef](#)]
27. Wang, X.; Zhang, M.; Liu, E.; He, F.; Shi, C.; He, C.; Li, J.; Zhao, N. Three-dimensional core-shell Fe_2O_3 @carbon/carbon cloth as binder-free anode for the high-performance lithium-ion batteries. *Appl. Surf. Sci.* **2016**, *390*, 350–356. [[CrossRef](#)]
28. Ma, C.; Zhang, W.; He, Y.S.; Gong, Q.; Che, H.; Ma, Z.F. Carbon coated SnO_2 nanoparticles anchored on CNT as a superior anode material for lithium-ion batteries. *Nanoscale* **2016**, *8*, 4121–4126. [[CrossRef](#)] [[PubMed](#)]
29. Guo, Q.; Qin, X. Flower-like SnO_2 nanoparticles grown on graphene as anode materials for lithium-ion batteries. *J. Solid State Electrochem.* **2013**, *18*, 1031–1039. [[CrossRef](#)]
30. Subramaniam, C.M.; Islam, M.M.; Akhter, T.; Cardillo, D.; Konstantinov, K.; Liu, H.K.; Dou, S.X. A chemically modified graphene oxide wrapped porous hematite nano-architecture as a high rate lithium-ion battery anode material. *RSC Adv.* **2016**, *6*, 82698–82706. [[CrossRef](#)]
31. Hu, J.; Zheng, J.; Tian, L.; Duan, Y.; Lin, L.; Cui, S.; Peng, H.; Liu, T.; Guo, H.; Wang, X.; et al. A core-shell nanohollow- $\gamma\text{-Fe}_2\text{O}_3$ @graphene hybrid prepared through the Kirkendall process as a high performance anode material for lithium ion batteries. *Chem. Commun.* **2015**, *51*, 7855–7858. [[CrossRef](#)] [[PubMed](#)]
32. Wang, H.; Xu, Z.; Yi, H.; Wei, H.; Guo, Z.; Wang, X. One-step preparation of single-crystalline Fe_2O_3 particles/graphene composite hydrogels as high performance anode materials for supercapacitors. *Nano Energy* **2014**, *7*, 86–96. [[CrossRef](#)]
33. Qin, X.; Zhang, H.; Wu, J.; Chu, X.; He, Y.-B.; Han, C.; Miao, C.; Wang, S.; Li, B.; Kang, F. Fe_3O_4 nanoparticles encapsulated in electrospun porous carbon fibers with a compact shell as high-performance anode for lithium ion batteries. *Carbon* **2015**, *87*, 347–356. [[CrossRef](#)]
34. Huang, Y.; Lin, Z.; Zheng, M.; Wang, T.; Yang, J.; Yuan, F.; Lu, X.; Liu, L.; Sun, D. Amorphous Fe_2O_3 nanoshells coated on carbonized bacterial cellulose nanofibers as a flexible anode for high-performance lithium ion batteries. *J. Power Sources* **2016**, *307*, 649–656. [[CrossRef](#)]
35. Li, Y.; Zhu, C.; Lu, T.; Guo, Z.; Zhang, D.; Ma, J.; Zhu, S. Simple fabrication of a Fe_2O_3 /carbon composite for use in a high-performance lithium ion battery. *Carbon* **2013**, *52*, 565–573. [[CrossRef](#)]
36. Mai, L.Q.; Yang, F.; Zhao, Y.L.; Xu, X.; Xu, L.; Luo, Y.Z. Hierarchical $\text{MnMoO}_4/\text{CoMoO}_4$ heterostructured nanowires with enhanced supercapacitor performance. *Nat. Commun.* **2011**, *2*. [[CrossRef](#)] [[PubMed](#)]
37. Kant, R. Theory for staircase voltammetry and linear scan voltammetry on fractal electrodes: Emergence of anomalous Randles-Sevcik behavior. *Electrochim. Acta* **2013**, *111*, 223–233.
38. Mundinamani, S.P.; Rabinal, M.K. Molecular modification of highly degenerate semiconductor as an active electrode to enhance the performance of supercapacitors. *Mater. Res. Express* **2014**, *1*, 045508. [[CrossRef](#)]
39. Nie, G.; Lu, X.; Lei, J.; Jiang, Z.; Wang, C. Electrospun V_2O_5 -doped $\alpha\text{-Fe}_2\text{O}_3$ composite nanotubes with tunable ferromagnetism for high-performance supercapacitor electrodes. *J. Mater. Chem. A* **2014**, *2*, 15495–15501. [[CrossRef](#)]

40. Nie, G.; Lu, X.; Chi, M.; Zhu, Y.; Yang, Z.; Song, N.; Wang, C. Hierarchical α -Fe₂O₃@MnO₂ core-shell nanotubes as electrode materials for high-performance supercapacitors. *Electrochim. Acta* **2017**, *231*, 36–43. [CrossRef]
41. Li, J.J.; Liu, M.C.; Kong, L.B.; Wang, D.; Hu, Y.M.; Han, W.; Kang, L. Advanced asymmetric supercapacitors based on Ni₃(PO₄)₂@GO and Fe₂O₃@GO electrodes with high specific capacitance and high energy density. *RSC Adv.* **2015**, *5*, 41721–41728. [CrossRef]
42. Tian, W.; Wang, X.; Zhi, C.; Zhai, T.; Liu, D.; Zhang, C.; Golberg, D.; Bando, Y. Ni(OH)₂ nanosheet@Fe₂O₃ nanowire hybrid composite arrays for high-performance supercapacitor electrodes. *Nano Energy* **2013**, *2*, 754–763. [CrossRef]
43. Xing, W.; Qiao, S.; Wu, X.; Gao, X.; Zhou, J.; Zhuo, S.; Hartono, S.B.; Hulicova-Jurcakova, D. Exaggerated capacitance using electrochemically active nickel foam as current collector in electrochemical measurement. *J. Power Sources* **2011**, *196*, 4123–4127. [CrossRef]
44. Zhu, X.; Zhu, Y.; Murali, S.; Stoller, M.D.; Ruoff, R.S. Nanostructured Reduced Graphene Oxide/Fe₂O₃ Composite As a High-Performance Anode Material for Lithium Ion Batteries. *ACS Nano* **2011**, *5*, 3333–3338. [CrossRef] [PubMed]
45. Fan, Z.; Yan, J.; Zhi, L.; Zhang, Q.; Wei, T.; Feng, J.; Zhang, M.; Qian, W.; Wei, F. A three-dimensional carbon nanotube/graphene sandwich and its application as electrode in supercapacitors. *Adv. Mater.* **2010**, *22*, 3723–3728. [CrossRef] [PubMed]
46. Wang, D.; Li, Y.; Wang, Q.; Wang, T. Nanostructured Fe₂O₃-graphene composite as a novel electrode material for supercapacitors. *J. Solid State Electrochem.* **2011**, *16*, 2095–2102. [CrossRef]
47. Shivakumara, S.; Penki, T.R.; Munichandraiah, N. Preparation and electrochemical performance of porous hematite (α -Fe₂O₃) nanostructures as supercapacitor electrode material. *J. Solid State Electrochem.* **2013**, *18*, 1057–1066. [CrossRef]
48. Zhao, P.; Li, W.; Wang, G.; Yu, B.; Li, X.; Bai, J.; Ren, Z. Facile hydrothermal fabrication of nitrogen-doped graphene/Fe₂O₃ composites as high performance electrode materials for supercapacitor. *J. Alloys Compd.* **2014**, *604*, 87–93. [CrossRef]
49. Li, J.; Zhang, W.; Zan, G.; Wu, Q. A high-performance dual-function material: Self-assembled super long α -Fe₂O₃ hollow tubes with multiple heteroatom (C-, N- and S-) doping. *Dalton Trans.* **2016**, *45*, 12790–12799. [CrossRef] [PubMed]
50. Liu, L.; Lang, J.; Zhang, P.; Hu, B.; Yan, X. Facile Synthesis of Fe₂O₃ Nano-Dots@Nitrogen-Doped Graphene for Supercapacitor Electrode with Ultralong Cycle Life in KOH Electrolyte. *ACS Appl. Mater. Interfaces* **2016**, *8*, 9335–9344. [CrossRef] [PubMed]
51. Zhang, M.; Sha, J.; Miao, X.; Liu, E.; Shi, C.; Li, J.; He, C.; Li, Q.; Zhao, N. Three-dimensional graphene anchored Fe₂O₃@C core-shell nanoparticles as supercapacitor electrodes. *J. Alloys Compd.* **2017**, *696*, 956–963. [CrossRef]
52. Nathan, D.M.G.T.; Boby, S.J.M. Hydrothermal preparation of hematite nanotubes/reduced graphene oxide nanocomposites as electrode material for high performance supercapacitors. *J. Alloys Compd.* **2017**, *700*, 67–74. [CrossRef]
53. Wang, D.; Dong, H.; Zhang, H.; Zhang, Y.; Xu, Y.; Zhao, C.; Sun, Y.; Zhou, N. Enabling a High Performance of Mesoporous α -Fe₂O₃ Anodes by Building a Conformal Coating of Cyclized-PAN Network. *ACS Appl. Mater. Interfaces* **2016**, *8*, 19524–19532. [CrossRef] [PubMed]

