

Article

Boosting Electrochemical Performance of Hematite Nanorods via Quenching-Induced Alkaline Earth Metal Ion Doping

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Abstract: Ion doping in transition metal oxides is always considered to be one of the most effective methods to obtain high-performance electrochemical supercapacitors because of the introduction of defective surfaces as well as the enhancement of electrical conductivity. Inspired by the smelting process, an ancient method, quenching is introduced for doping metal ions into transition metal oxides with intriguing physicochemical properties. Herein, as a proof of concept, α -Fe₂O₃ nanorods grown on carbon cloths (α -Fe₂O₃@CC) heated at 400 °C are rapidly put into different aqueous solutions of alkaline earth metal salts at 4 °C to obtain electrodes doped with different alkaline earth metal ions (M-Fe₂O₃@CC). Among them, Sr-Fe₂O₃@CC shows the best electrochemical capacitance, reaching 77.81 mF cm⁻² at the current of 0.5 mA cm⁻², which is 2.5 times that of α -Fe₂O₃@CC. The results demonstrate that quenching is a feasible new idea for improving the electrochemical performances of nanostructured materials.

Keywords: quenching; alkaline earth metals; doping; hematite nanorods; supercapacitors



Citation: Chen, Q.; Chong, Y.; Rao, M.; Su, M.; Qiu, Y. Boosting Electrochemical Performance of Hematite Nanorods via Quenching-Induced Alkaline Earth Metal Ion Doping. *Processes* **2021**, *9*, 1102. <https://doi.org/10.3390/pr9071102>

Academic Editor: Adina Arvinte

Received: 29 May 2021

Accepted: 22 June 2021

Published: 24 June 2021

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1. Introduction

At present, the main electrode material of the commercial supercapacitor is still carbon material. However, the surface sites of the carbon-based material cannot be fully utilized, which causes the actual specific capacitance of the electric double layer capacitors (EDLC) to be far less than the theoretical value. Therefore, the energy density of commercial supercapacitors based on the EDLC is not ideal [1]. The nanostructured transition metal active materials have more active sites for faraday redox reaction at the electrode/electrolyte interface to enhance charge storage and, thus, exhibit excellent pseudocapacitance as well as energy density [2,3]; these materials include CoO_x [4], MnO₂ [5–7], RuO₂ [8,9], etc.

α -Fe₂O₃ is considered as a good candidate for the electrode material of supercapacitors owing to its multivalent state, negative potential window, and high theoretical capacitance [10]. However, the poor conductivity of α -Fe₂O₃ ($\sim 10^{-14}$ S cm⁻¹) limits the actual capacitance [11,12]. Further, the carbon-based materials have high electric conductivity (2–12 S cm⁻¹) [13]. Therefore, in order to solve the above limitations, researchers have proposed different solutions. For α -Fe₂O₃ carbon composite materials, Wang et al. anchored α -Fe₂O₃ nanoparticles on nitrogen-containing graphene, using the superior specific surface area and high conductivity of graphene to increase the ion transmission rate, so that the pseudocapacitance of α -Fe₂O₃ can be fully utilized [14]. Babasaheb R. Sankapal et al. deposited multiwalled carbon nanotubes (MWCNTs) on a stainless steel sheet and then dipped it into a precursor solution to adsorb Fe³⁺. After annealing, α -Fe₂O₃/MWCNTs with high conductivity was obtained [15]. To modify the structure, N. Munichandraiah

et al. used a porous ball structure to embed α -Fe₂O₃, increasing the specific surface area of α -Fe₂O₃ and overcoming the defect of low conductivity [16]. Additionally, Wang et al. successfully prepared V₂O₅-decorated α -Fe₂O₃ composite nanotubes by electrospinning, which shows better reaction reversibility and cycle stability [17].

The conductivity of α -Fe₂O₃ is critical to increase its pseudocapacitance [18]. As we know, doping can enhance the conductivity and increase oxygen vacancies of nanomaterials. Specially, alkaline earth metal ion doping will affect the band structure and carrier migration rate. M.V. Reddy et al. [19] synthesized Mg-doped α -Fe₂O₃ electrode materials for the anode of lithium-ion batteries. After 50 charge–discharge cycles, the capacity retention rate was higher and the capacity decay was lower than that of the control sample. Chen et al. [20] improved the oxygen reduction reaction (ORR) performance by doping with alkaline earth metals (Mg, Ca, etc.). Guo et al. [21] used Ca-doped α -Fe₂O₃ to purify peroxymonosulfate (PMS) in wastewater. Ca doping can not only enhance the electron transfer rate from α -Fe₂O₃ to PMS but also increase the specific surface area of α -Fe₂O₃. Here, we have developed a new doping method, quenching, which is widely used in steel manufacturing to change the physical properties of iron. Generally, the iron blocks burning at high temperature are quickly immersed in a solution at a low temperature. In this paper, this method results in more surface defects of as-synthesized materials when the quenching solution is deionized water. The disorganization may further lead to doping of alkaline earth metal ions when the solution is the corresponding alkaline earth metal salt solution [22]. The improved electrochemical performance can be obtained without complex processes. α -Fe₂O₃ is directly grown on carbon cloths (CC) without additional binders and carbon black. During the conversion of FeOOH to α -Fe₂O₃, the scorching-hot α -Fe₂O₃ was quickly put into different alkaline earth metal salt solutions. α -Fe₂O₃@CC was quenched into Mg(NO₃)₂, Ca(NO₃)₂, Sr(NO₃)₂, and Ba(NO₃)₂ solutions, respectively. Mg²⁺, Ca²⁺, Sr²⁺, and Ba²⁺ ions can be successfully doped into α -Fe₂O₃ nanorods. The influence of these four alkaline earth metal ions on the capacitance performance of α -Fe₂O₃ has also been explored. Among them, Sr-Fe₂O₃@CC shows the best results, reaching 77.81 mF cm^{−2} at the current of 0.5 mA cm^{−2}.

2. Materials and Methods

2.1. Materials

FeCl₃ and Na₂SO₄ of analytical grade were purchased from Shanghai Aladdin Bio-Technology Co., Ltd. (Shanghai, China). Sr(NO₃)₂, Ba(NO₃)₂, Mg(NO₃)₂, and Ca(NO₃)₂ of analytical grade were purchased from Guangzhou Chemical Reagent Factory Co., Ltd. (Guangzhou, China).

2.2. Fabrication of α -Fe₂O₃@CC

α -Fe₂O₃@CC was synthesized by traditional hydrothermal method (Figure S2). In short, 0.946 g FeCl₃ and 0.497 g Na₂SO₄ were dissolved in 70 mL deionized water under stirring for 30 min at room temperature. The solution was then transferred to 100 mL autoclave liners, and two pieces of 2 × 3 cm² CC were vertically immersed into the reaction solution and kept sealed at 160 °C for 6 h. After the reaction, the CC coated with a yellow product was washed with deionized water and ethanol for several times and dried at 70 °C for 12 h. The obtained precursor FeOOH was calcined in a muffle furnace at 400 °C for 1 h to obtain α -Fe₂O₃@CC.

2.3. Fabrication of Sr-Fe₂O₃@CC

The solution of Sr(NO₃)₂ was prepared by dissolving 3.704 g of Sr(NO₃)₂ in 35 mL of deionized water. After stirring at room temperature for 30 min, the solution was transferred to a refrigerator at 4 °C for 6 h.

The precursor was prepared in the same way. After roasting in a muffle furnace at 400 °C for 1 h, the sample was rapidly put into the prepared Sr(NO₃)₂ solution for

quenching, washed three times with deionized water and ethanol, and then dried at 70 °C for 12 h to obtain Sr-Fe₂O₃@CC.

2.4. Fabrication of Ba-Fe₂O₃@CC

The solution of Ba(NO₃)₂ was prepared by dissolving 4.575 g of Ba(NO₃)₂ in 35 mL of deionized water. After stirring at room temperature for 30 min, the solution was transferred to a refrigerator at 4 °C for 6 h. The precursor and quenching were prepared in the same way to obtain Ba-Fe₂O₃@CC.

2.5. Fabrication of Mg-Fe₂O₃@CC

The solution of Mg(NO₃)₂ was prepared by dissolving 4.487 g of Mg(NO₃)₂ in 35 mL of deionized water. After stirring at room temperature for 30 min, the solution was transferred to a refrigerator at 4 °C for 6 h. The precursor and quenching were prepared in the same way to obtain Mg-Fe₂O₃@CC.

2.6. Fabrication of Ca-Fe₂O₃@CC

The solution of Ca(NO₃)₂ was prepared by dissolving 4.132 g of Ca(NO₃)₂ in 35 mL of deionized water. After stirring at room temperature for 30 min, the solution was transferred to a refrigerator at 4 °C for 6 h. The precursor and quenching were prepared in the same way to obtain Ca-Fe₂O₃@CC.

2.7. Characterization

Sample morphologies were examined by SEM (ZEISS, Germany, 5.0 kV). The latter was equipped with EDS mapping capabilities. XRD patterns were collected on an X-ray diffractometer (X'Pert Powder, Netherlands) equipped with a Cu K α radiation source ($\lambda_1 = 1.54060$ Å, $\lambda_2 = 1.54442$ Å). XRD patterns were collected over the range $2\theta = 10$ – 90° at a scanning rate of 5° min^{-1} and a step size of 0.01° . Raman spectroscopy (Alpha300 R Raman Instruments, Germany) was introduced to measure materials by using an excitation laser of 532 nm. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo Scientific K-Alpha spectrometer (America) equipped with a monochromatic Al K α X-ray source (1486.6 eV) operating at 100 W. Adventitious hydrocarbon reference (C 1s = 284.8 eV) was used for binding energy scale calibration. Bulk elemental compositions were examined using ICP-OES (Agilent ICP-OES 730, America). O₂-TPD analyses were carried out on a TP-5080B (China) multifunctional adsorption apparatus equipped with a TCD detector. A 50 mg catalyst was pre-treated at 300 °C for 1 h in 30 mL min^{-1} He flow. The gas was switched to 10% O₂/He at a flow rate of 30 mL min^{-1} for 30 min, and the O₂-TPD curves were collected from 50 to 700 °C with a linear heating rate of $10^\circ \text{ C min}^{-1}$ in the flow of He gas at 30 mL min^{-1} .

2.8. Electrochemical Measurements

The electrochemical performance of the M-Fe₂O₃@CC was characterized using a Biologic electrochemical workstation. In half-cell tests, the electrochemical measurements were performed in a standard three-electrode cell with an aqueous 5 M LiCl solution as the electrolyte, a platinum foil as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. The working electrode consists of M-Fe₂O₃@CC (carbon cloth, $1.0 \text{ cm} \times 1.0 \text{ cm}$, Figure S3).

3. Results

3.1. Characterization

Figure 1 shows the scanning electron microscope (SEM) images of Mg-Fe₂O₃@CC, Ca-Fe₂O₃@CC, Sr-Fe₂O₃@CC, and Ba-Fe₂O₃@CC. The SEM image of hematite supported on CC is shown in Figure S4. All four samples had similar morphology. SEM images at different magnifications confirm that the quenched α -Fe₂O₃ had good coverage and was evenly distributed on the surface of CC. It can be seen that the rapid quenching process did

not cause the detachment or aggregation of α -Fe₂O₃ nanorods, and this characteristic still remained with the change of quenching solution, so nanomaterials doped with different alkaline earth metal ions can be obtained. α -Fe₂O₃ was supported on CC in the form of a one-dimensional nanorod array (Figure 1a), which not only provides a large electrochemically active surface, but also facilitates the rapid transfer of electrons and ions [23]. It is noted that the doping amounts of ions were different after quenching. When the quenching solution concentration was 0.5 mol/L, the doping amounts of Sr²⁺, Ba²⁺, Mg²⁺, and Ca²⁺ were 0.34 wt.%, 1.30 wt.%, 0.17 wt.%, and 0.9 wt.% respectively (Table 1), which may be related to the radius and electronegativity of ions.

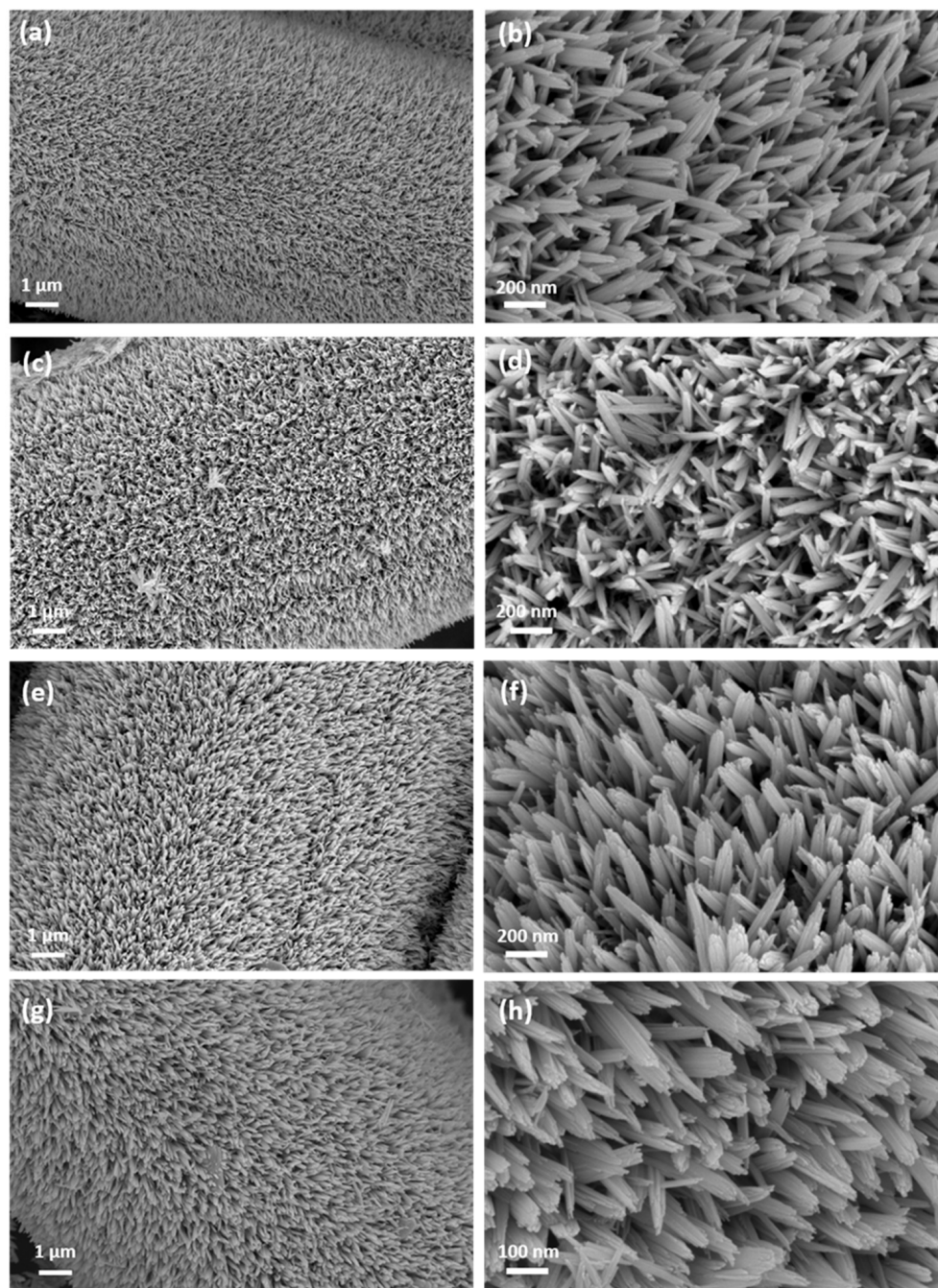


Figure 1. SEM images of (a,b) Sr-Fe₂O₃@CC, (c,d) Ba-Fe₂O₃@CC, (e,f) Mg-Fe₂O₃@CC, and (g,h) Ca-Fe₂O₃@CC.

Table 1. The content of Sr^{2+} , Ba^{2+} , Mg^{2+} , and Ca^{2+} in $\text{Sr-Fe}_2\text{O}_3@\text{CC}$, $\text{Ba-Fe}_2\text{O}_3@\text{CC}$, $\text{Mg-Fe}_2\text{O}_3@\text{CC}$, and $\text{Ca-Fe}_2\text{O}_3@\text{CC}$ according to the ICP-OES measurement.

Sample	M^{2+} (mg/Kg)	M^{2+} (wt. %)
$\text{Sr-Fe}_2\text{O}_3@\text{CC}$	3365	0.34
$\text{Ba-Fe}_2\text{O}_3@\text{CC}$	12,965	1.30
$\text{Mg-Fe}_2\text{O}_3@\text{CC}$	1691	0.17
$\text{Ca-Fe}_2\text{O}_3@\text{CC}$	9023	0.90

Figure 2a exhibits the X-ray diffraction (XRD) pattern of the FeOOH precursor. The position and relative intensity of the diffraction peak matched with the JCPDS card of FeOOH (#75-1594) [24]. The diffraction peaks in the XRD pattern (Figure 2b) of $\alpha\text{-Fe}_2\text{O}_3$ easily matched the hematite phase (JCPDS#33-0664), $2\theta = 24.01^\circ$, 33.18° , 35.60° , 40.73° , 49.38° , 54.01° , and 62.32° , corresponding to the crystal planes (012), (104), (110), (113), (024), (116), (214), and (300), respectively [25], which shows that the modification of Sr^{2+} , Ba^{2+} , Mg^{2+} , and Ca^{2+} did not significantly change the crystal structure of $\alpha\text{-Fe}_2\text{O}_3$. However, it is difficult to detect the different diffraction peaks after quenching attributed to the small amounts of ions doping.

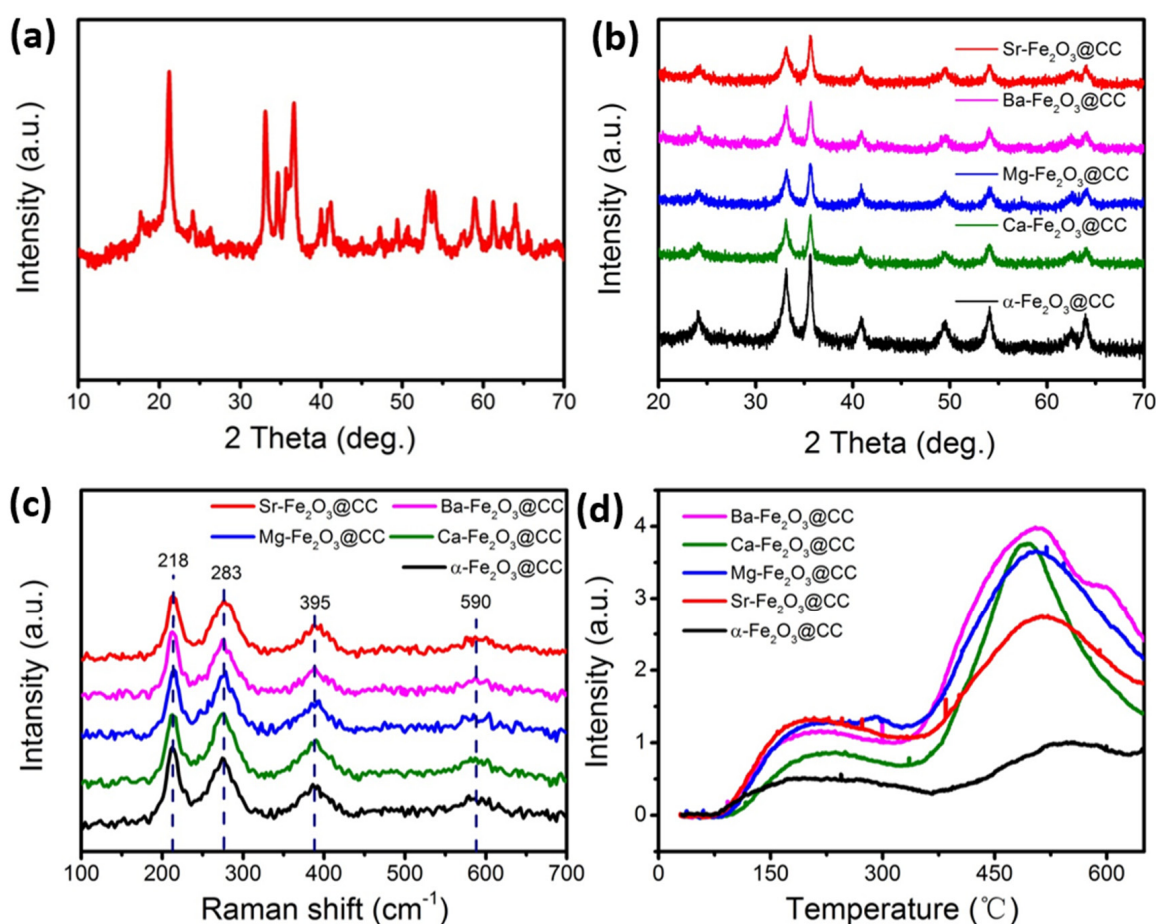


Figure 2. (a) XRD patterns for FeOOH . (b) XRD patterns, (c) Raman spectra, and (d) O_2 -TPD patterns for $\alpha\text{-Fe}_2\text{O}_3@\text{CC}$, $\text{Sr-Fe}_2\text{O}_3@\text{CC}$, $\text{Ba-Fe}_2\text{O}_3@\text{CC}$, $\text{Mg-Fe}_2\text{O}_3@\text{CC}$, and $\text{Ca-Fe}_2\text{O}_3@\text{CC}$.

Figure 2c shows the Raman spectra collected for $\alpha\text{-Fe}_2\text{O}_3@\text{CC}$, $\text{Sr-Fe}_2\text{O}_3@\text{CC}$, $\text{Ba-Fe}_2\text{O}_3@\text{CC}$, $\text{Mg-Fe}_2\text{O}_3@\text{CC}$, and $\text{Ca-Fe}_2\text{O}_3@\text{CC}$ [26,27]. It is found that the Raman spectra of all the samples were almost unchanged after quenching treatment, which may be due to the low doping amounts. O_2 temperature-programmed desorption (O_2 -TPD) is used to

determine the concentration of oxygen vacancies [28]. The conductivity of the electrode material is related to the property of surface oxygen and the form of the oxygen species adsorbed on the surface. It can be identified by the following transformation reaction: O_2 (adsorption) $\rightarrow O^{2-}$ (adsorption) $\rightarrow O^-$ (adsorption) $\rightarrow O^{2-}$ (adsorption/lattice) [29]. The first peak ($\sim 250^\circ C$) is related to the desorption of physically adsorbed oxygen. The second peak ($\sim 500^\circ C$) is related to the chemical desorption of O^{2-} (and/or O^-). The third peak ($< 600^\circ C$) is related to the desorption of lattice oxygen. It can be seen from Figure 2d that the area of the second peak increased in all samples after quenching in alkaline earth metal solution, which means an increase in oxygen defects. Among them, the area of the second peak of $Ba-Fe_2O_3@CC$ increased the most, while $Sr-Fe_2O_3@CC$ increased the least. On the one hand, the increase in oxygen vacancies is conducive to the improvement of electrical conductivity. The capacitance also is affected by doping amount, electrochemical specific surface area (ECSA), and other factors, so comprehensive analysis is needed.

The X-ray photoelectron spectroscopy (XPS) survey spectra for $Sr-Fe_2O_3@CC$ are shown in Figure 3a, revealing the presence of Sr in $Sr-Fe_2O_3@CC$. Furthermore, the Sr 3d XPS spectrum in Figure 3b shows the presence of satellite peaks 134.70 and 136.80 eV for Sr^{2+} [30,31].

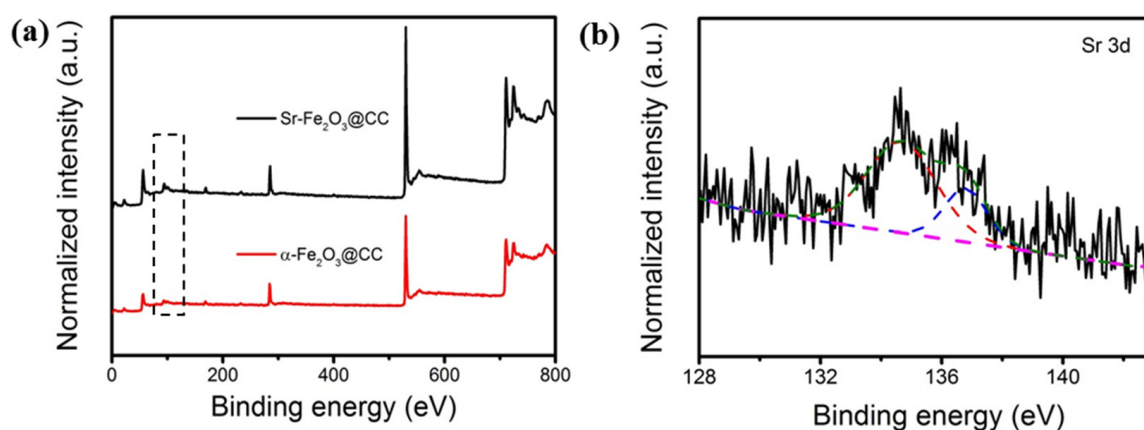


Figure 3. (a) XPS survey spectra of $\alpha-Fe_2O_3@CC$ and $Sr-Fe_2O_3@CC$. (b) Sr 3d core-level XPS spectra for $Sr-Fe_2O_3@CC$.

The specific Brunauer–Emmett–Teller (BET) surface area of the sample is slightly different due to alkaline earth metal ions doping after quenching (Table 2) [32]. The Nitrogen adsorption/desorption isotherms are shown in Figure S5. Compared with the undoped $\alpha-Fe_2O_3@CC$, the specific surface area of $Sr-Fe_2O_3@CC$ increased from $77.18\text{ m}^2\text{ g}^{-1}$ to $79.60\text{ m}^2\text{ g}^{-1}$, which may be due to the defective surface caused by Sr^{2+} doping [33]. The specific surface area of the $Ba-Fe_2O_3@CC$ sample was reduced by $74.65\text{ m}^2\text{ g}^{-1}$. The specific surface area of $Mg-Fe_2O_3@CC$ was almost unchanged due to the low doping amount [34]. The specific surface area of $Ca-Fe_2O_3@CC$ was greatly reduced by $53.06\text{ m}^2\text{ g}^{-1}$, which may be related to the pore destruction of $\alpha-Fe_2O_3$ caused by the doping of Ca^{2+} .

Table 2. BET surface area for $\alpha-Fe_2O_3@CC$, $Sr-Fe_2O_3@CC$, $Ba-Fe_2O_3@CC$, $Mg-Fe_2O_3@CC$, and $Ca-Fe_2O_3@CC$.

Sample	BET Surface Area ($\text{m}^2\text{ g}^{-1}$)
$\alpha-Fe_2O_3@CC$	77.18
$Sr-Fe_2O_3@CC$	79.60
$Ba-Fe_2O_3@CC$	74.65
$Mg-Fe_2O_3@CC$	77.52
$Ca-Fe_2O_3@CC$	53.06

The increase in the ECSA enhances the contact area between the electrode and electrolyte and then increases the accumulation of charge [34]. To further explore the factors that affect the increase in capacitance, the ECSA was determined by measuring the electric double layer capacitance (C_{DL}) from the CV curve at various scan rates, shown in Figure 4, and the ECSA value was determined by the slope of i_c - v , shown in Table 3. After doping with alkaline earth metal ions, the ECSA of all samples improved, except for Ca-Fe₂O₃@CC. The doping of Sr²⁺ ions can induce the change of nanostructured surface of α -Fe₂O₃, leading to generation of more active sites and the increase in the ECSA. The ECSA of Sr-Fe₂O₃@CC reached twice that of α -Fe₂O₃@CC, which can result in a substantial improvement in the capacitance of Sr-Fe₂O₃@CC. Table 3 shows the ECSA value of Ca-Fe₂O₃@CC. It can be seen that after Ca²⁺ doping, the ECSA of α -Fe₂O₃@CC dropped by 98%. Ca²⁺ ions can affect the inner surface potential, changing the surface charge due to their adsorption and formation the Stern plane in the EDL. Therefore, Ca²⁺ may induce particle coagulation, which may destroy the pore structure of the material surface, resulting in a decrease in BET and ECSA [35]. Therefore, the ability of α -Fe₂O₃ to transport electrons and store charges is reduced.

3.2. Electrochemical Performances of M-Fe₂O₃@CC Electrode

In order to explore the electrochemical properties of the materials before and after quenching, cyclic voltammetry (CV) and galvanostatic charge–discharge (GCD) tests were carried out in a standard three-electrode system with M-Fe₂O₃@CC as the working electrode, the platinum mesh as the counter electrode, and an SCE as the reference electrode, tested in 5 M LiCl solution.

Figure 5a shows the CV curves of different electrodes collected at a scan rate of 100 mV s^{−1}. The current density of the Sr-Fe₂O₃@CC electrode was significantly higher than those of the unquenched α -Fe₂O₃@CC electrode and the α -Fe₂O₃@CC electrode doped with Ba²⁺, Mg²⁺, and Ca²⁺, indicating that the Sr²⁺ modification was the most effective form in the four alkaline earth metal ions [36]. This is because, with the doping of Sr²⁺ ions, the ECSA increases, which greatly increases the EDLC of Sr-Fe₂O₃@CC. At the same time, the increase in oxygen vacancies enhances the electron and ion transfer rate between the electrode and electrolyte, which accelerates the rate of redox reactions and greatly increases the pseudocapacitance. The capacitance of the Ca-Fe₂O₃@CC electrode was significantly smaller than that of the original α -Fe₂O₃@CC, which proves that the modification of Ca²⁺ has a side effect on α -Fe₂O₃@CC. In addition, the shape of the CV curve (Figure 5a) was also different from other electrodes. This may be due to the fact that the surface structure breaks after Ca²⁺ doping. At the same time, its ability for electron adsorption and charge storage decreased with the reduction in ECSA, resulting in a decrease in EDLC, both of which make the final capacitance reduce massively.

Figure 5b shows the GCD curves of Sr-Fe₂O₃@CC, Ba-Fe₂O₃@CC, Mg-Fe₂O₃@CC, and Ca-Fe₂O₃@CC collected at a current density of 1 mA cm^{−2}. Sr-Fe₂O₃@CC exhibited the highest area capacitance among all tested electrodes, reaching 77.81 mF cm^{−2} at 0.5 mA cm^{−2}. When the current density increased from 0.5 mA cm^{−2} to 8 mA cm^{−2} (Figure 5c), the charge–discharge curve of Sr-Fe₂O₃@CC maintained an equilateral triangle shape, indicating that Sr-Fe₂O₃@CC has excellent capacitance and faraday reaction reversibility [37]. When tested at high current density (8 mA cm^{−2}), a capacitance of 67.34% was maintained (Figure 5d). The EIS curve (Figure 5e) shows that the Sr-Fe₂O₃@CC had the lowest equivalent series resistance [38]. For supercapacitors, stability is an important consideration. Figure 5f shows that Ba-Fe₂O₃@CC, Mg-Fe₂O₃@CC, and Sr-Fe₂O₃@CC possessed good cycling stability and had no downward trend (a capacitance of 100% of the initial capacitance maintain) after 800 charge–discharge cycles at the current density of 1 mA cm^{−2}. However, the initial capacity was relatively low, and it needed to be activated for a period of time.

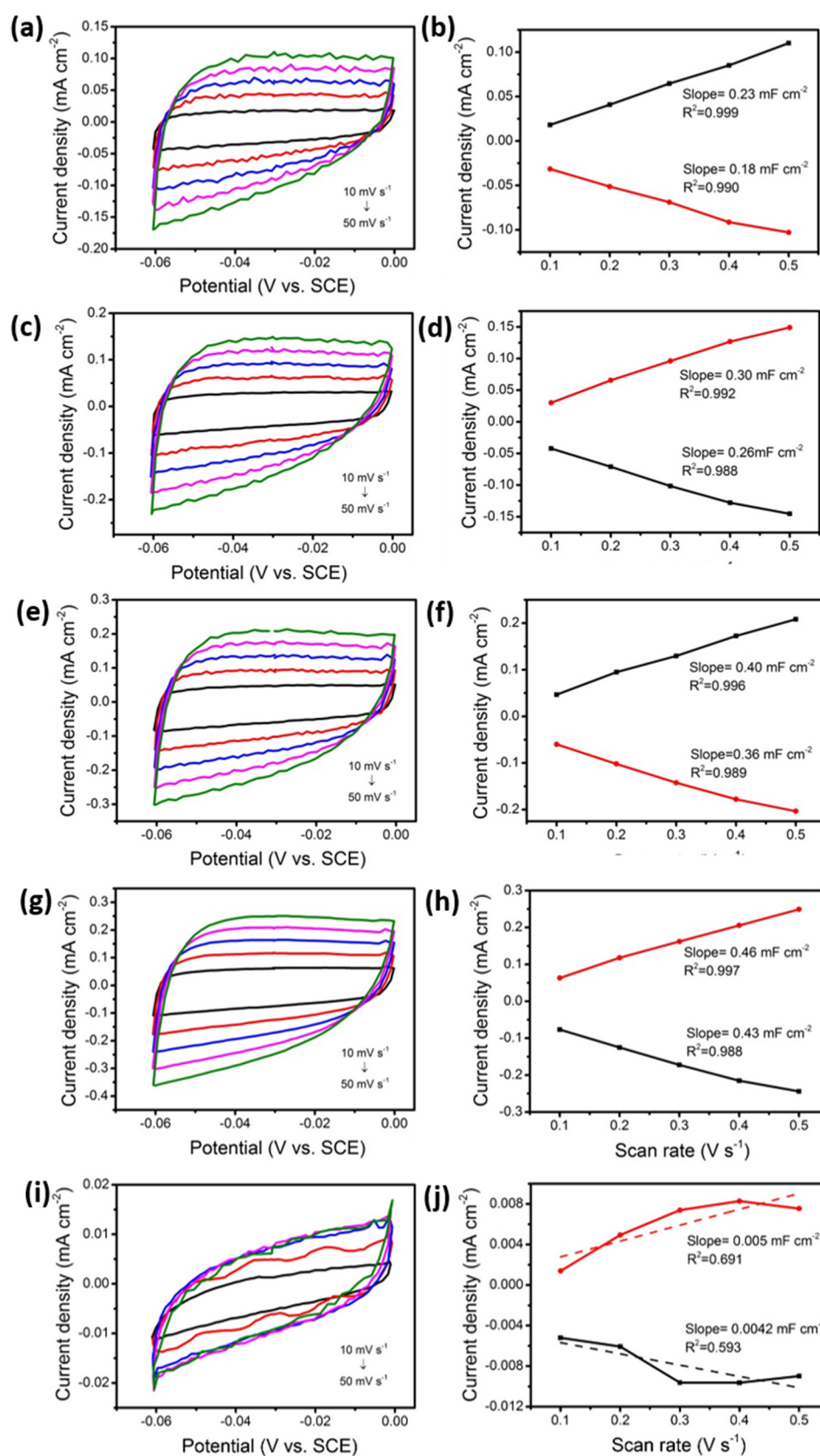


Figure 4. CV curves in non-Faradaic region and the ratio of cathodic/anodic current with various scan rates of (a,b) $\alpha\text{-Fe}_2\text{O}_3@\text{CC}$, (c,d) $\text{Ba-Fe}_2\text{O}_3@\text{CC}$, (e,f) $\text{Mg-Fe}_2\text{O}_3@\text{CC}$, (g,h) $\text{Sr-Fe}_2\text{O}_3@\text{CC}$, and (i,j) $\text{Ca-Fe}_2\text{O}_3@\text{CC}$.

Table 3. ECSA for α -Fe₂O₃@CC, Sr-Fe₂O₃@CC, Ba-Fe₂O₃@CC, Mg-Fe₂O₃@CC, and Ca-Fe₂O₃@CC.

Sample	C _{DL} (mF)	ECSA (cm ²)
α -Fe ₂ O ₃ @CC	0.2050	5.12
Sr-Fe ₂ O ₃ @CC	0.4450	11.13
Ba-Fe ₂ O ₃ @CC	0.2800	7.00
Mg-Fe ₂ O ₃ @CC	0.3800	9.50
Ca-Fe ₂ O ₃ @CC	0.0046	0.12

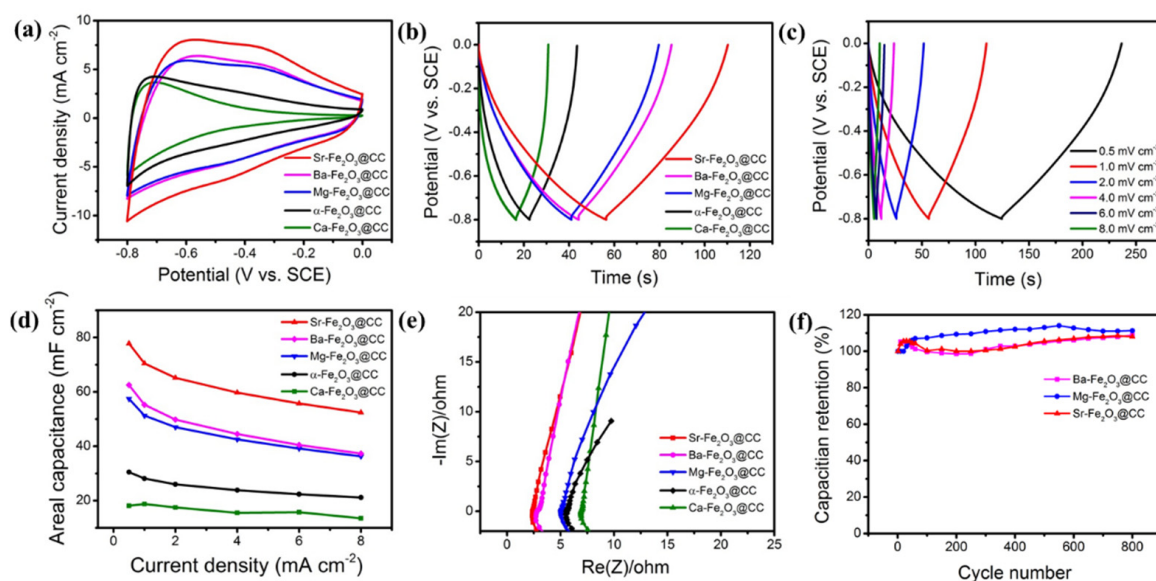


Figure 5. (a) CV curves collected at a scan rate of 100 mV s^{−1} for Sr-Fe₂O₃@CC, Ba-Fe₂O₃@CC, Mg-Fe₂O₃@CC, α -Fe₂O₃@CC, and Ca-Fe₂O₃@CC. (b) GCD curves collected at a current density of 1 mA cm^{−2} for Sr-Fe₂O₃@CC, Ba-Fe₂O₃@CC, Mg-Fe₂O₃@CC, and Ca-Fe₂O₃@CC. (c) GCD curves for the Sr-Fe₂O₃@CC electrode collected at different current densities. (d) Specific areal capacitances and (e) EIS curves for Sr-Fe₂O₃@CC, Ba-Fe₂O₃@CC, Mg-Fe₂O₃@CC, and Ca-Fe₂O₃@CC at different current densities. (f) Cycling stability for Ba-Fe₂O₃@CC, Mg-Fe₂O₃@CC, and Sr-Fe₂O₃@CC at a current density of 1 mA cm^{−2}.

3.3. Formatting of Mathematical Components

The areal capacitance (C_s) in the three-electrode cell was calculated according to Equation (1):

$$C_s = \frac{I \times \Delta t}{s \times \Delta v} \quad (1)$$

where I is the discharge current, Δt is the discharge time, s is the electrode area, v is the electrode volume, and Δv is the potential. The area of the M-Fe₂O₃@CC fiber is about 1 cm².

Cyclic voltammetry curves were collected in 1 M NaOH at different scan rates. The electrochemical specific surface areas of Sr-Fe₂O₃@CC, Ba-Fe₂O₃@CC, Mg-Fe₂O₃@CC, and Ca-Fe₂O₃@CC electrodes were tested under −0.06 V to 0.00 V (relative to SCE). The double-layer current (i_c) is equal to the product of the scan rate (v) and the electrochemical double-layer capacitance (C_{DL}), as shown in Equation (2):

$$i_c = vC_{DL} \quad (2)$$

The slope value of the i_c - v fitted line (Figure 3b,d,f,h,i) is equal to C_{DL} . The ECSA value was obtained through calculation according to Equation (3):

$$\text{ECSA} = \frac{C_{DL}}{C_s} \quad (3)$$

where C_s is the specific capacitance, which is $40.00 \mu\text{F cm}^{-2}$ for general metal oxides.

4. Conclusions

In summary, we introduced a new method, quenching, to modify the surfaces of nano-materials for improving electrochemical performance of $\alpha\text{-Fe}_2\text{O}_3$ nanorods. $\alpha\text{-Fe}_2\text{O}_3\text{@CC}$ was quenched in $\text{Sr}(\text{NO}_3)_2$, $\text{Ba}(\text{NO}_3)_2$, $\text{Mg}(\text{NO}_3)_2$, and $\text{Ca}(\text{NO}_3)_2$ solutions, and Sr^{2+} , Ba^{2+} , Mg^{2+} , and Ca^{2+} ions were successfully doped into $\alpha\text{-Fe}_2\text{O}_3$ nanorods. The doping amounts of ions varies with the different ionic radius and valence of the ions. The $\text{Sr-Fe}_2\text{O}_3\text{@CC}$ electrode achieved the best performance, reaching 77.81 mF cm^{-2} at 0.5 mA cm^{-2} . Due to the doping of Sr^{2+} , the ECSA increases, which greatly increases the EDLC of $\text{Sr-Fe}_2\text{O}_3\text{@CC}$. Besides, the increase in oxygen vacancies accelerates the electron and ion transfer rate between the electrode and electrolyte, resulting in the increase in the pseudocapacitance. It is interesting to note that the modification of Ca^{2+} has the opposite effect. The capacitance of $\text{Ca-Fe}_2\text{O}_3\text{@CC}$ has decreased, which proves that not all ion modifications can have a positive effect on the capacitance of supercapacitors. The function needs to be selected according to the properties of the ion itself, such as radius, redox, and so on.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/pr9071102/s1>, Figure S1: Digital photo of (a) the thickness (b) length and width of carbon cloth. (c,d) SEM images of carbon cloth in different magnifications., Figure S2. Schematic of hydrothermal reaction. Figure S3. Schematic of three electrode test. Figure S4. SEM image of hematite supported on CC. Figure S5. Nitrogen adsorption/desorption isotherms for $\alpha\text{-Fe}_2\text{O}_3\text{@CC}$, $\text{Sr-Fe}_2\text{O}_3\text{@CC}$, $\text{Ba-Fe}_2\text{O}_3\text{@CC}$, $\text{Mg-Fe}_2\text{O}_3\text{@CC}$ and $\text{Ca-Fe}_2\text{O}_3\text{@CC}$.

Author Contributions: Conceptualization and methodology, Y.Q. and M.R.; data curation, Q.C. and M.S.; writing—original draft preparation, Q.C. and M.S.; writing—review and editing, M.S. and Y.C.; project administration, Y.Q.; funding acquisition, Y.Q. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by National Key Research and Development Program of China (2018YFA0209600), Science and Technology Key Project of Guangdong Province, China (2020B010188002), Guangdong Innovative and Entrepreneurial Research Team Program (2019ZT08L075), Foshan Innovative and Entrepreneurial Research Team Program (2018IT100031), Guangdong Pearl River Talent Program (2019QN01L054), Shenzhen Peacock Plan (KQTD2016053015544057) and Nanshan Pilot Plan (LHTD20170001), Science and Technology Program of Guangzhou, China (202002030153), the Guangdong Science and Technology Program (2017B030314002), National Natural Science Foundation of China (52000076), Innovation and Entrepreneurship Talent Program of Shaoguan City, China Postdoctoral Science Foundation (2020M682714) and the Fundamental Research Funds for the Central Universities (2020ZYGXZR061).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Zhang, L.L.; Zhao, X.S. Carbon-based materials as supercapacitor electrodes. *Chem. Soc. Rev.* **2009**, *38*, 2520–2531. [CrossRef] [PubMed]
2. Chen, D.; Zhou, S.; Quan, H.; Zou, R.; Gao, W.; Luo, X.; Guo, L. Tetra-subo-like $\alpha\text{-Fe}_2\text{O}_3/\text{C}$ nanoarrays on carbon cloth as negative electrode for high-performance asymmetric supercapacitors. *Chem. Eng. J.* **2018**, *341*, 102–111. [CrossRef]
3. Choudhury, A.; Kim, J.-H.; Yang, K.-S.; Yang, D.-J. Facile synthesis of self-standing binder-free vanadium pentoxide-carbon nanofiber composites for high-performance supercapacitors. *Electrochim. Acta* **2016**, *213*, 400–407. [CrossRef]
4. Kandalkar, S.G.; Gunjekar, J.L.; Lokhande, C.D. Preparation of cobalt oxide thin films and its use in supercapacitor application. *Appl. Surf. Sci.* **2008**, *254*, 5540–5544. [CrossRef]

5. Huang, H.; Wang, X.; Tervoort, E.; Zeng, G.; Liu, T.; Chen, X.; Sologubenko, A.; Niederberger, M. Nano-Sized Structurally Disordered Metal Oxide Composite Aerogels as High-Power Anodes in Hybrid Supercapacitors. *ACS Nano* **2018**, *12*, 2753–2763. [[CrossRef](#)] [[PubMed](#)]
6. Wei, W.; Cui, X.; Chen, W.; Ivey, D.G. Manganese oxide-based materials as electrochemical supercapacitor electrodes. *Chem. Soc. Rev.* **2011**, *40*, 1697–1721. [[CrossRef](#)] [[PubMed](#)]
7. Jyothibas, J.P.; Wang, R.-H.; Ong, K.; Ong, J.H.L.; Lee, R.-H. Cellulose/carbon nanotube/MnO₂ composite electrodes with high mass loadings for symmetric supercapacitors. *Cellulose* **2021**, *28*, 3549–3567. [[CrossRef](#)]
8. Xia, H.; Shirley Meng, Y.; Yuan, G.; Cui, C.; Lu, L. A Symmetric RuO₂/RuO₂ Supercapacitor Operating at 1.6 V by Using a Neutral Aqueous Electrolyte. *Electrochem. Solid State Lett.* **2012**, *15*, A60–A63. [[CrossRef](#)]
9. Jiang, Q.; Kurra, N.; Alhabeb, M.; Gogotsi, Y.; Alshareef, H.N. All Pseudocapacitive MXene–RuO₂ Asymmetric Supercapacitors. *Adv. Energy Mater.* **2018**, *8*, 1703043. [[CrossRef](#)]
10. Yang, Z.; Qiu, A.; Ma, J.; Chen, M. Conducting α -Fe₂O₃ nanorod/polyaniline/CNT gel framework for high performance anodes towards supercapacitors. *Compos. Sci. Technol.* **2018**, *156*, 231–237. [[CrossRef](#)]
11. Li, Y.; Xu, J.; Feng, T.; Yao, Q.; Xie, J.; Xia, H. Fe₂O₃ Nanoneedles on Ultrafine Nickel Nanotube Arrays as Efficient Anode for High-Performance Asymmetric Supercapacitors. *Adv. Funct. Mater.* **2017**, *27*, 1606728. [[CrossRef](#)]
12. Owusu, K.A.; Qu, L.; Li, J.; Wang, Z.; Zhao, K.; Yang, C.; Hercule, K.M.; Lin, C.; Shi, C.; Wei, Q.; et al. Low-crystalline iron oxide hydroxide nanoparticle anode for high-performance supercapacitors. *Nat. Commun.* **2017**, *8*, 14264. [[CrossRef](#)] [[PubMed](#)]
13. Zhang, X.; Wang, Q.; Xia, X.; He, W.; Huang, X.; Logan, B.E. Addition of conductive particles to improve the performance of activated carbon air-cathodes in microbial fuel cells. *Environ. Sci. Water Res. Technol.* **2017**, *3*, 806–810. [[CrossRef](#)]
14. Ma, Z.; Huang, X.; Dou, S.; Wu, J.; Wang, S. One-Pot Synthesis of Fe₂O₃ Nanoparticles on Nitrogen-Doped Graphene as Advanced Supercapacitor Electrode Materials. *J. Phys. Chem. C* **2014**, *118*, 17231–17239. [[CrossRef](#)]
15. Raut, S.S.; Sankapal, B.R. Comparative studies on MWCNTs, Fe₂O₃ and Fe₂O₃/MWCNTs thin films towards supercapacitor application. *New J. Chem.* **2016**, *40*, 2619–2627. [[CrossRef](#)]
16. Shivakumara, S.; Penki, T.R.; Munichandraiah, N. Synthesis and Characterization of Porous Flowerlike Fe₂O₃ Nanostructures for Supercapacitor Application. *ECS Electrochem. Lett.* **2013**, *2*, A60–A62. [[CrossRef](#)]
17. Nie, G.; Lu, X.; Lei, J.; Jiang, Z.; Wang, C. Electrospun V₂O₅-doped α -Fe₂O₃ composite nanotubes with tunable ferromagnetism for high-performance supercapacitor electrodes. *J. Mater. Chem. A* **2014**, *2*, 15495–15501. [[CrossRef](#)]
18. Ni, C.; Hou, J.; Li, L.; Li, Y.; Wang, M.; Yin, H.; Tan, W.J.C. The remarkable effect of alkali earth metal ion on the catalytic activity of OMS-2 for benzene oxidation. *Chemosphere* **2020**, *250*, 126211. [[CrossRef](#)]
19. Reddy, M.V.; Yao, Q.C.; Adams, S. Mg, Cu, Zn doped Fe₂O₃ as an electrode material for Li-ion batteries. *Mater. Lett.* **2018**, *2*, 186–192. [[CrossRef](#)]
20. Liu, S.; Li, Z.; Wang, C.; Tao, W.; Huang, M.; Zuo, M.; Yang, Y.; Yang, K.; Zhang, L.; Chen, S.; et al. Turning main-group element magnesium into a highly active electrocatalyst for oxygen reduction reaction. *Nat. Commun.* **2020**, *11*, 938. [[CrossRef](#)] [[PubMed](#)]
21. Guo, S.; Wang, H.; Yang, W.; Fida, H.; You, L.; Zhou, K. Scalable synthesis of Ca-doped α -Fe₂O₃ with abundant oxygen vacancies for enhanced degradation of organic pollutants through peroxymonosulfate activation. *Appl. Catal. B Environ.* **2020**, *2*, 118250. [[CrossRef](#)]
22. Su, M.; Pan, Z.; Chong, Y.; Ye, C.; Jin, X.; Wu, Q.; Hu, Z.; Ye, D.; Waterhouse, G.I.N.; Qiu, Y.; et al. Boosting the electrochemical performance of hematite nanorods via quenching-induced metal single atom functionalization. *J. Mater. Chem. A* **2021**, *9*, 3492–3499. [[CrossRef](#)]
23. Poornajar, M.; Nguyen, N.; Ahn, H.-J.; Büchler, M.; Liu, N.; Kment, S.; Zboril, R.; Yoo, J.; Schmuki, P. Fe₂O₃ Blocking Layer Produced by Cyclic Voltammetry Leads to Improved Photoelectrochemical Performance of Hematite Nanorods. *Surfaces* **2019**, *2*, 131–144. [[CrossRef](#)]
24. Bouhjar, F.; Derbali, L.; Marí, B.; Bessaïs, B. Electrodeposited Cr-Doped α -Fe₂O₃ thin films active for photoelectrochemical water splitting. *Int. J. Hydrog. Energy* **2020**, *45*, 11492–11501. [[CrossRef](#)]
25. Kumar, P.; Sharma, P.; Shrivastav, R.; Dass, S.; Satsangi, V.R. Electrodeposited zirconium-doped α -Fe₂O₃ thin film for photoelectrochemical water splitting. *Int. J. Hydrog. Energy* **2011**, *36*, 2777–2784. [[CrossRef](#)]
26. Shen, S.; Guo, P.; Wheeler, D.A.; Jiang, J.; Lindley, S.A.; Kronawitter, C.X.; Zhang, J.Z.; Guo, L.; Mao, S.S. Physical and photoelectrochemical properties of Zr-doped hematite nanorod arrays. *Nanoscale* **2013**, *5*, 9867. [[CrossRef](#)]
27. Shen, S.; Jiang, J.; Guo, P.; Kronawitter, C.X.; Mao, S.S.; Guo, L. Effect of Cr doping on the photoelectrochemical performance of hematite nanorod photoanodes. *Nano Energy* **2012**, *1*, 732–741. [[CrossRef](#)]
28. Wu, Y.; Dong, L.; Li, B. Effect of iron on physicochemical properties: Enhanced catalytic performance for novel Fe₂O₃ modified CuO/Ti_{0.5}Sn_{0.5}O₂ in low temperature CO oxidation. *Mol. Catal.* **2018**, *456*, 65–74. [[CrossRef](#)]
29. Ayastuy, J.L.; Gurbani, A.; Gutiérrez-Ortiz, M.A. Effect of calcination temperature on catalytic properties of Au/Fe₂O₃ catalysts in CO-PROX. *Int. J. Hydrog. Energy* **2016**, *41*, 19546–19555. [[CrossRef](#)]
30. Li, M.; Liu, H.; Zhu, H.; Gao, H.; Zhang, S.; Chen, T. Kinetics and mechanism of Sr(II) adsorption by Al-Fe₂O₃: Evidence from XPS analysis. *J. Mol. Liq.* **2017**, *2*, 364–369. [[CrossRef](#)]
31. Komai, S.; Hirano, M.; Ohtsu, N. Spectral analysis of Sr 3d XPS spectrum in Sr-containing hydroxyapatite. *Surf. Interface Anal.* **2020**, *52*, 823–828. [[CrossRef](#)]

32. Wang, Y.; Wang, Y.; Cao, J.; Kong, F.; Xia, H.; Zhang, J.; Zhu, B.; Wang, S.; Wu, S. Low-temperature H₂S sensors based on Ag-doped α -Fe₂O₃ nanoparticles. *Sens. Actuators B Chem.* **2008**, *131*, 183–189. [[CrossRef](#)]
33. Banerjee, A.M.; Shirole, A.R.; Pai, M.R.; Tripathi, A.K.; Bharadwaj, S.R.; Das, D.; Sinha, P.K. Catalytic activities of Fe₂O₃ and chromium doped Fe₂O₃ for sulfuric acid decomposition reaction in an integrated boiler, preheater, and catalytic decomposer. *Appl. Catal. B Environ.* **2012**, *127*, 36–46. [[CrossRef](#)]
34. Zhao, X.; Meng, J.; Yan, Z.; Cheng, F.; Chen, J. Nanostructured NiMoO₄ as active electrocatalyst for oxygen evolution. *Chin. Chem. Lett.* **2019**, *30*, 319–323. [[CrossRef](#)]
35. Szymanek, K.; Charmas, R.; Piasecki, W. A study on the mechanism of Ca⁽²⁺⁾ adsorption on TiO₂ and Fe₂O₃ with the usage of calcium ion-selective electrode. *Chemosphere* **2020**, *242*, 125162. [[CrossRef](#)] [[PubMed](#)]
36. Liu, D.; Zhao, X.; Su, R.; Hao, Z.; Jia, B.; Li, S.; Dong, L. Highly Porous Graphitic Activated Carbons from Lignite via Microwave Pretreatment and Iron-Catalyzed Graphitization at Low-Temperature for Supercapacitor Electrode Materials. *Processes* **2019**, *7*, 300. [[CrossRef](#)]
37. Jiang, J.; Liu, X.X.; Han, J.; Hu, K.; Chen, J.S. Self-Supported Sheets-on-Wire CuO@Ni(OH)₂/Zn(OH)₂ Nanoarrays for High-Performance Flexible Quasi-Solid-State Supercapacitor. *Processes* **2021**, *9*, 680. [[CrossRef](#)]
38. Zeng, Y.; Han, Y.; Zhao, Y.; Zeng, Y.; Yu, M.; Liu, Y.; Tang, H.; Tong, Y.; Lu, X. Advanced Ti-Doped Fe₂O₃@PEDOT Core/Shell Anode for High-Energy Asymmetric Supercapacitors. *Adv. Energy Mater.* **2015**, *5*, 1402176. [[CrossRef](#)]