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## Research Article

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# High-energy supercapacitor constructed of La-doped $\text{ZnFe}_2\text{O}_4$ positive electrode material and hydrophilic carbon nanotube negative electrode

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**Abstract:** In this work, lanthanum was adopted to modify zinc ferrite. Using La-doped  $\text{ZnFe}_2\text{O}_4$  as cathode and hydrophilic carbon nanotubes as anode, a high-energy-density asymmetric supercapacitor was fabricated. Flaky  $\text{ZnFe}_2\text{O}_4$  was synthesized via sol-gel and hydrothermal methods, and La doping was realized by microwave-assisted treatment. The optimal doping time was 12 h with a La doping content of 0.5%. Hydrophilic carbon nanotubes were prepared by arc discharge and acid-base treatment. Material characterizations verified that 0.5% La- $\text{ZnFe}_2\text{O}_4$  possessed favorable microstructure and a large specific surface area of 114.8  $\text{m}^2/\text{g}$ , while carbon nanotubes exhibited superior wettability owing to abundant hydrophilic groups. Electrochemical tests in 2 M KOH electrolyte revealed that 0.5% La- $\text{ZnFe}_2\text{O}_4$  delivered a high specific capacitance of 426 F/g with outstanding rate capability, and its energy storage was dominated by surface-controlled pseudocapacitance with a contribution ratio of 68%. The assembled asymmetric device presented stable cycling performance with 83.2% capacitance retention after 10,000 cycles at 10 A/g, and achieved superior energy and power densities. This study provides a reliable experimental reference for developing advanced supercapacitor electrode materials.

**Keywords:** Thin films;  $\text{ZnFe}_2\text{O}_4$  material; Supercapacitor; La element; Carbon nanotubes

## 1. Introduction

In the context of continued global economic growth and expanding population, excessive consumption of fossil energy has not only aggravated the problem of energy shortage, but also brought about a series of serious challenges such as climate change and environmental pollution[ 1, 2]. Therefore, vigorously developing green, sustainable and clean energy has become a top priority. Supercapacitors are widely used in portable electronic equipment, aerospace, new energy vehicles and other fields due to their outstanding advantages such as fast charge and discharge rates, wide operating temperature range, and high safety. However, current supercapacitors generally have shortcomings of low energy density, which makes it difficult to meet the increasing needs of practical applications. Therefore, the development of new electrode materials suitable for asymmetric supercapacitors conforms to the development direction of energy storage technology and has important theoretical significance and engineering application value. According to the charge storage mechanism, supercapacitors can be mainly divided into two categories: electric double layer capacitors and pseudocapacitors. Pseudocapacitors realize charge storage through the redox reaction on the surface of the electrode material, which can significantly improve the capacitance and energy

density. The asymmetric structure can further optimize the overall energy storage performance of the device[3–5]. The electrochemical performance and catalytic activity of materials are highly dependent on their microscopic morphology and structure. Multi-level nanostructures such as nanosheets, nanorods, nanoneedles, and nanotubes can effectively increase the specific surface area, provide sufficient ion transmission channels and reaction sites, enhance electrolyte wettability, and shorten the ion diffusion distance, thereby significantly improving the electrochemical performance and application prospects of electrode materials. It can be seen that the design and optimization of electrode materials are the key to promoting the advancement of supercapacitor technology[6, 7].

Previous studies have shown that zinc ferrite ( $\text{ZnFe}_2\text{O}_4$ ) is a promising supercapacitor electrode material, and its electrochemical performance can be significantly improved through element doping modification[8–10]. Li Wenchao doped the transition metal V into  $\text{ZnFe}_2\text{O}_4$ , and the prepared electrode showed high specific capacity and excellent cycle stability in energy storage tests[11, 12]; Zhang Hexin successfully induced the generation of oxygen vacancies by preliminary doping  $\text{ZnFe}_2\text{O}_4$  with La, effectively improving the electrocatalytic and energy storage properties of the material[13]; Gao Ya used Co doping to destroy the zinc ferrite lattice structure to increase the specific surface area of the material. Different from existing research, this study uses La doping modification, which not only destroys the zinc ferrite lattice, but also significantly increases the oxygen vacancy content, thereby more efficiently improving the electrochemical performance of the material. In order to accurately optimize its energy storage performance, this study uses  $\text{ZnFe}_2\text{O}_4$  as a matrix and constructs a disordered porous sheet-like La- $\text{ZnFe}_2\text{O}_4$  material through La doping to introduce rich redox active sites and improve conductivity. Rare earth La has outstanding performance in  $\text{ZnFe}_2\text{O}_4$  doping modification due to its unique electronic configuration and excellent chemical activity. It can effectively regulate its key properties such as crystal structure and oxygen vacancies, and solve bottlenecks such as poor conductivity and insufficient active sites of pure phase  $\text{ZnFe}_2\text{O}_4$ .  $\text{ZnFe}_2\text{O}_4$  itself has the advantages of high specific capacity and environmental friendliness. Combined with the regulatory effect of La doping, it can maximize the energy storage performance of supercapacitors and further optimize the comprehensive electrochemical performance of zinc ferrite-based materials. In this study, hydrophilic carbon nanotubes were used as the negative electrode. This material shows many outstanding advantages when applied to the negative electrode and can fully meet the needs of electrochemical energy storage. The rich hydrophilic groups on its surface can effectively optimize the wetting effect between the electrode and the electrolyte, significantly reduce the interface contact resistance, and thereby accelerate the migration and transmission efficiency of lithium ions. In addition, the unique hollow tubular structure of hydrophilic carbon nanotubes not only provides sufficient active sites and smooth channels for the insertion and extraction of lithium ions, but also effectively buffers the volume expansion effect of the material during charge and discharge cycles, significantly improving the cycle stability of the electrode. At the same time, the material itself has excellent conductive properties, which can effectively enhance the electronic conduction efficiency inside the electrode. Coupled with its good chemical stability, it further ensures the safety and rate performance of the battery during long-term charge and discharge processes, and can well meet the needs of high-capacity and long-life electrochemical energy storage applications[14–18].

To sum up, this study first prepared a high-purity  $\text{ZnFe}_2\text{O}_4$  material, and then used doping time and La element doping ratio as key variables, combined with a series of characterization analysis

methods to screen out the doped products with the best performance. On this basis, we further used the optimal La-ZnFe<sub>2</sub>O<sub>4</sub> as the positive electrode material and hydrophilic carbon nanotubes as the negative electrode material to build a high-performance supercapacitor, and systematically studied the electrochemical performance of the device.

## 2. Experimental preparation

### 2.1 Preparation of ZnFe<sub>2</sub>O<sub>4</sub> and La-ZnFe<sub>2</sub>O<sub>4</sub> materials

Weigh 2.5 g zinc nitrate hexahydrate and 1.23 g ferric nitrate tetrahydrate, place them together in a container containing 40 mL deionized water, and use a magnetic stirrer to continue stirring at 300 rpm for 30 min until the two reagents are completely dissolved to obtain a uniform mixed solution. Then, add 25% ammonia water to the mixed solution drop by drop, stirring while adding, to accurately control the pH value of the solution within the range of 3 to 4. Then add 10 mL of ethylene glycol, place the container in a 60 °C water bath environment, and continue magnetic stirring for 2 h until a transparent and uniform sol is formed. Transfer the prepared transparent sol to a clean sealed container, heat the container to 80 °C and keep it at a constant temperature, and let it stand for 12 h to allow the sol to fully undergo a gelation reaction to form a gel. After the gel is generated, disperse it into 30 mL of deionized water, add an appropriate amount of hexamethylenetetramine (HMT), and stir magnetically for 30 min to ensure that the system is evenly mixed. Transfer the above mixture to a high-pressure reactor lined with polytetrafluoroethylene and react at a constant temperature of 180 °C for 11 h. After the reaction is completed, turn off the heating device and allow the reactor to naturally cool to room temperature. The reaction product was washed three times by alternating centrifugation with deionized water and absolute ethanol to completely remove the precursors and other impurities that did not participate in the reaction. After washing, the product was placed in a 60 °C oven to dry for 12 h to obtain flake precursor powder. Finally, put the flaky precursor powder into a muffle furnace, set the calcination temperature to 800 °C, and calcine at a constant temperature for 2 h. After the calcination is completed, it is naturally cooled to room temperature to obtain the flaky ZnFe<sub>2</sub>O<sub>4</sub> material[13, 19]. The preparation process is shown in (Figure 1).

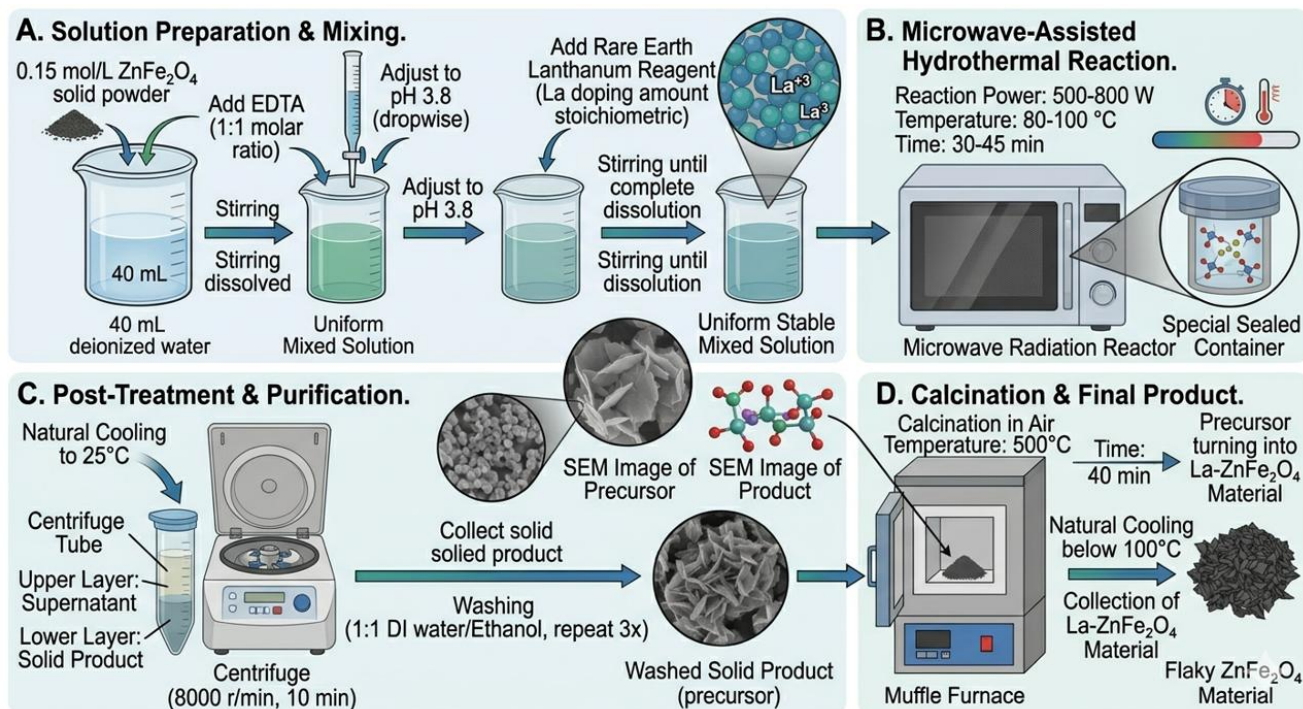


Figure 1. Flow chart for the preparation of  $\text{ZnFe}_2\text{O}_4$ .

Take an appropriate amount of  $\text{ZnFe}_2\text{O}_4$  solid powder, add deionized water and stir thoroughly until completely dissolved. Prepare a  $0.15 \text{ mol L}^{-1}$   $\text{ZnFe}_2\text{O}_4$  aqueous solution. Adjust the pH value of the system to 3.8; add the EDTA complexing agent drop by drop according to a molar ratio of 1:1 and continue stirring until the complexing agent is completely dissolved, then add a measured amount of rare earth lanthanum reagent (so that the La doping amount meets the stoichiometric requirements of the target product), continue stirring until all reagents are completely dissolved, forming a uniform and stable mixed solution. Transfer the mixed solution to a special container of the microwave radiation reactor. After sealing the container, set the reaction power to 500–800 W, the reaction temperature to 80–100 °C, and the reaction time to 30–45 min, and start the microwave-assisted reaction program. After the reaction is completed, wait for the system to naturally cool to 25 °C, transfer the reaction mixture to a centrifuge tube,

mixture to a centrifuge tube, and centrifuge at 8000 rpm for 10 min to collect the solid product in the lower layer of the centrifuge tube; alternately wash the solid product with a 1:1 mixture of deionized water and absolute ethanol, and repeat washing three times to completely remove unreacted precursors and impurities. Finally, the washed solid product is put into a muffle furnace and roasted in an air atmosphere at 500 °C for 40 min. After the temperature in the furnace is cooled to below 100 °C, the product is taken out, which is La-doped zinc ferrite (La- $\text{ZnFe}_2\text{O}_4$ ) material. The yield is 84.7%. The preparation flow chart is shown in (Figure 2).

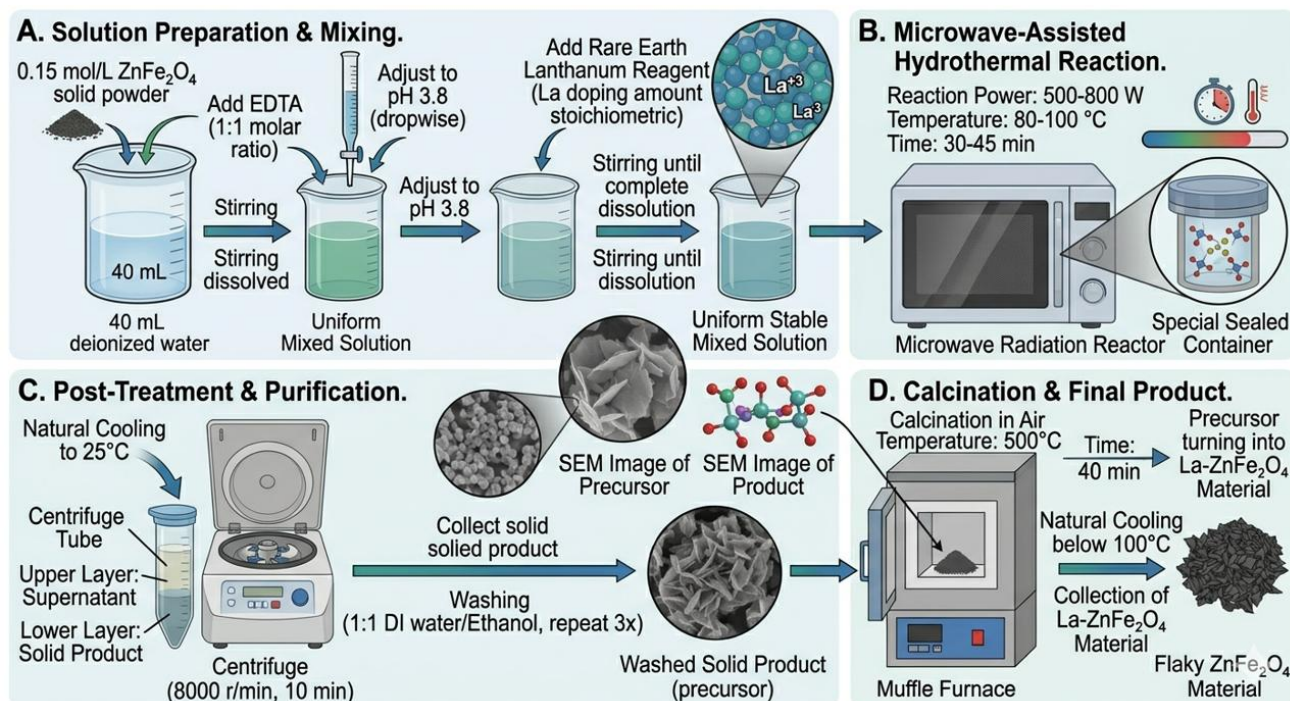


Figure 2. Flow chart for the preparation of  $\text{La-ZnFe}_2\text{O}_4$  nanosheets.

## 2.2 Preparation of hydrophilic carbon nanotubes

As shown in (Figure 3), carbon nanotubes (CNTs) are prepared using the arc discharge method: high-purity graphite rods with a purity of 99.99% are used as the carbon source, the reaction chamber is evacuated and filled with high-purity argon with a purity of  $\geq 99.999\%$ , and the arc discharge parameters are adjusted to maintain a deposition temperature of 500–800 °C to promote carbon source deposition and produce high-crystallinity carbon nanotubes with a production yield of 76.3%. Hydrophilic modification was then carried out: 250 mg of carbon nanotubes were weighed and added to 50 mL of deionized water to prepare a suspension of  $5 \text{ mg mL}^{-1}$ . After stirring, dispersion and ultrasonic treatment, the carbon nanotube powder was obtained by drying. The powder was placed in a tube furnace, passed in argon gas with a flow rate of 80 sccm, heated to 500 °C at a heating rate of 5 °C/min and treated at a constant temperature to remove surface impurities. After cooling, add  $1\text{--}2 \text{ mol L}^{-1}$  NaOH solution to adjust the pH of the system to 12.5, then add dropwise 30%  $\text{H}_2\text{O}_2$  solution with a volume ratio of 10:1, react at room temperature and dry until semi-dry; then use  $1\text{--}2 \text{ mol L}^{-1}$  HCl solution (pH = 1.2) for pickling, and repeatedly wash with deionized water until the system pH = 7.0, repeat this purification process five times, and finally dried to obtain hydrophilic carbon nanotube materials. The yield after modification was 87.6% (Figure 3)

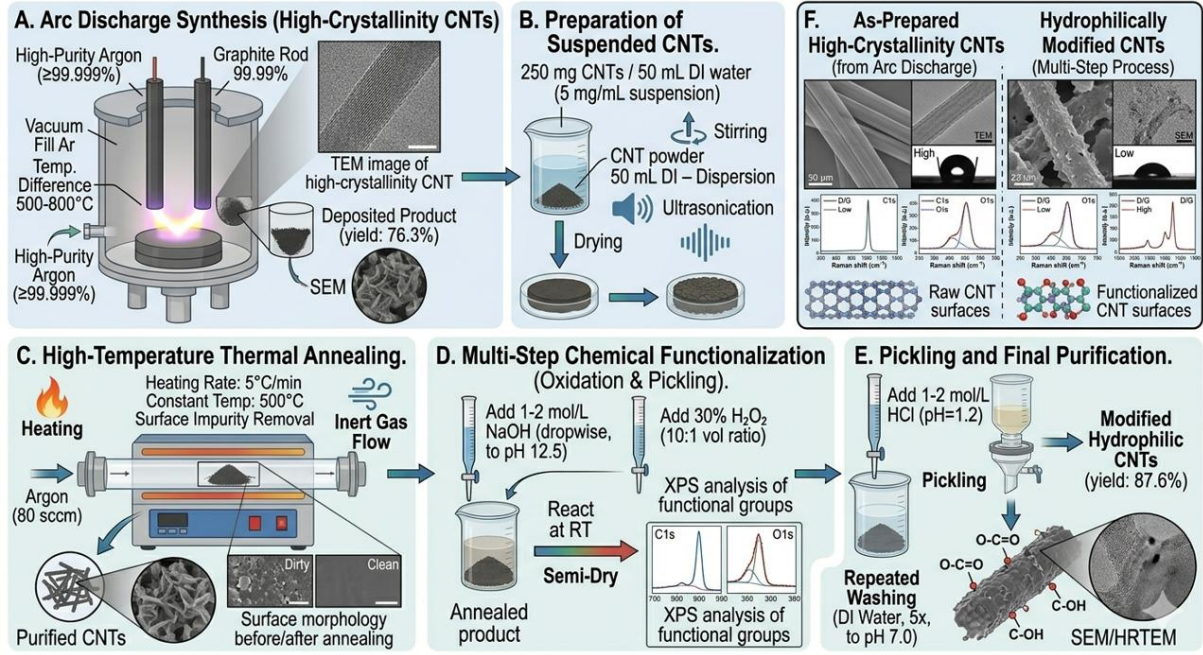


Figure 3. Flow chart for the preparation of hydrophilic carbon nanotubes.

### 2.3 Related formulas

The formulas required in the experiment are as follows:

$$C_s = \frac{it}{mV} \quad (1)$$

$$P = \frac{3600E}{\Delta t} \quad (2)$$

$$E = 0.5C_s\Delta V^2 \quad (3)$$

$C_s$  (F/g) represents the specific capacitance,  $\Delta t$  (s) represents the discharge time,  $i$  (A) represents the current density,  $\Delta V$  (V) represents the voltage drop during the discharge process,  $m$  (g) represents the mass of the active material,  $P$  (W/kg) represents the power density, and  $E$  (Wh/kg) represents the energy density.

$$i = k_1v + k_2v^{1/2} \quad (4)$$

$$i = av^b \quad (5)$$

Here,  $i$  and  $v$  represent the peak current and scan rate, respectively.  $a$  is a constant, and  $b$  is derived from the functional relationship between  $\log(i)$  and  $\log(v)$ .  $k_1v$  and  $k_2v^{1/2}$  represent the surface-controlled capacitive contribution and the diffusion-controlled contribution, respectively.

## 2.4 Experimental equipment

The equipment used during the experiment is shown in Table 1 below.

Table 1. List of instruments required for the experimental process.

| Name (Instrument)                      | Model            | Manufacturer                                                  |
|----------------------------------------|------------------|---------------------------------------------------------------|
| Electronic Balance                     | WLC.X2           | Gansu Ruide Biotechnology Co., Ltd.                           |
| Magnetic Stirrer                       | H03-B            | Shanghai Meiyongpu Instrument & Meter Manufacturing Co., Ltd. |
| Forced Air Drying Oven                 | DHG-9053A        | Shanghai Yiheng Scientific Instruments Co., Ltd.              |
| Scanning Electron Microscope (SEM)     | NOVA NANOSEM 430 | FEI Company (USA)                                             |
| Transmission Electron Microscope (TEM) | JEM-2100F        | JEOL Ltd. (Japan)                                             |
| X-ray Diffractometer (XRD)             | Empyrean         | Malvern Panalytical Ltd.                                      |
| Electrochemical Workstation            | CHI660E          | Shanghai Chenhua Instrument Co., Ltd.                         |
| Sonicator                              | Q500             | Shanghai Murong Biotechnology Co., Ltd.                       |
| Jacketed Glass Reactor                 | GJR—05L          | Shanghai Yuanhuai Technology Co., Ltd.                        |

The main raw materials used during the experiment are shown in Table 2 below.

Table 2. List of main raw materials for the experiment.

| Name                        | Molecular Formula                                    | Manufacturer                            |
|-----------------------------|------------------------------------------------------|-----------------------------------------|
| Zinc Nitrate Hexahydrate    | $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ | Wuhan Jiyesheng Chemical Co., Ltd.      |
| Ferric Nitrate Tetrahydrate | $\text{Fe}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$ | Wuhan Jiyesheng Chemical Co., Ltd.      |
| Ammonia Water               | $\text{NH}_3 \cdot \text{H}_2\text{O}$               | Jining Mike Rare Earth Co., Ltd.        |
| Ethylene Glycol             | $\text{C}_2\text{H}_6\text{O}_2$                     | Guangdong Guanghua Technology Co., Ltd. |
| Anhydrous Ethanol           | $\text{C}_2\text{H}_5\text{OH}$                      | Pani Chemical Reagents                  |

### 3. Characterization of physical properties of $\text{ZnFe}_2\text{O}_4$ and $\text{La-ZnFe}_2\text{O}_4$ nanosheet electrodes

The microstructure of the material plays a crucial role in its electrochemical performance. For this reason, this study focuses on the optimal reaction conditions during the preparation of electrode materials. Figure 4(a–d) shows the microstructure evolution rules of  $\text{La-ZnFe}_2\text{O}_4$  under different doping reaction times. Among them, Figure 4a shows the SEM morphology of the sample when the reaction took place for 2 h. At this time, the reaction was not fully carried out. The material was nanospherical and had a smooth surface. The specific surface area was low and it was unable to provide sufficient active sites for electrochemical reactions. Figure 4(b–d) are high-magnification SEM images of reactions for 8 h, 12 h and 16 h respectively. They all formed interlaced lamellar nanostructures with similar overall morphologies. The nanosheet structure can effectively shorten the electron transmission distance and improve the electron conduction efficiency; and as the reaction time prolongs, the surface roughness of the material gradually increases, and a large number of fine particles are attached to the nanosheets to form a layered structure, which is beneficial to accelerating the migration rate of ions in the electrolyte. It is worth noting that the reaction time has little effect on the length and width of the nanosheets. This is mainly due to the fact that La doping destroys the regular structure of the original crystal and makes the material size relatively stable. Specifically, in Figure 4c (reaction 12 h), the thickness of the nanosheet increases and convex structures appear on the surface, further improving the specific surface area and specific capacitance performance; at the same time, La doping transforms the originally disordered nanosheets into an ordered arrangement, increasing the contact area between the electrode and the electrolyte, increasing redox active sites, and creating favorable conditions for rapid charge transfer. In Figure 4d (reaction 16 h), the sample shows obvious overgrowth, and the structural disorder increases significantly, accompanied by severe lattice fractures and defects. The stacking of nanosheets leads to a decrease in crystallinity and poor chemical stability. The lattice defects also destroy the structural integrity, which is not conducive to stable electron transmission and improvement of electrochemical performance. Combined with the analysis of the structure-activity relationship between microscopic morphology and performance, it was determined that 12 h was the optimal time for the  $\text{La-ZnFe}_2\text{O}_4$  doping reaction. Samples prepared under this condition were used in subsequent experiments.

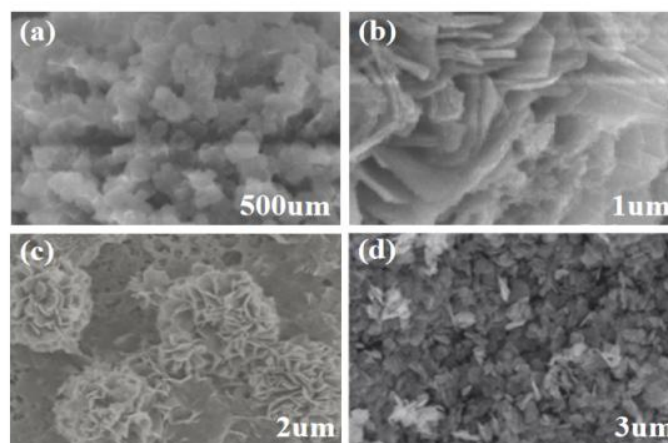


Figure 4. (a–d) High-power SEM images of La-ZnFe<sub>2</sub>O<sub>4</sub> at 2, 8, 12 and 16 h.

After discovering the effect of reaction time on the micromorphology of La-ZnFe<sub>2</sub>O<sub>4</sub>, this study further systematically analyzed the influence of different La doping ratios on the microstructure of the material. The relevant characterization results are shown in (Figure 5). Experimental results show that as the La doping concentration gradually increases, when it reaches a certain threshold, the grain size and deposition amount of the material tend to stabilize. This result confirms that the incorporation of La element does not change the inherent closing characteristics of the ZnFe<sub>2</sub>O<sub>4</sub> matrix itself. The SEM morphology under different doping ratios is analyzed as follows: Figure 5(a) shows the microstructure of pure phase ZnFe<sub>2</sub>O<sub>4</sub>. It can be seen that a large number of nanosheets are intertwined and stacked seriously, and the overall arrangement is chaotic. At the same time, there are mesoporous structures and rib-like morphologies in the material. Figure 5(b) shows the morphology of the sample when the La doping amount is 0.2%. Compared with pure ZnFe<sub>2</sub>O<sub>4</sub>, the specific surface area of the material at this doping ratio is significantly increased, providing more ample interface space for efficient electrochemical reactions. When the La doping amount is 0.5%, La-ZnFe<sub>2</sub>O<sub>4</sub> exhibits optimal micromorphological characteristics: obvious adhesion occurs on the surface of the nanosheet structure, and the surface roughness of the nanosheets is greatly increased. This morphological evolution further increases the specific surface area of the material, effectively increasing the number of active sites for electrochemical reactions. The intrinsic mechanism is that the secondary growth phase migrates to the lattice cracks and adheres in situ, effectively restraining the extension of the initial lattice defects, and ultimately optimizing the surface structure of the material. As shown in (Figure 5d), if the La doping ratio continues to increase, although the surface roughness of the nanosheets is still increasing, serious agglomeration and stacking occurs between the nanosheets. Instead, the specific surface area of the material no longer increases or even decreases, and the number of redox active sites also decreases. The reason is that excess La ions will replace Zn ions in the crystal lattice, inducing lattice distortion and nanosheet fragmentation; and as the doping amount continues to increase, the degree of crystal lattice damage continues to intensify, and the reaction process is more likely to reduce the specific surface area through nanosheet cracking and fragmentation, ultimately leading to the attenuation of the electrochemical performance of the material. Based on the analysis of the morphology-property structure-activity relationship under different La doping ratios, it was determined that 0.5% is the optimal doping ratio of La-ZnFe<sub>2</sub>O<sub>4</sub>, and subsequent relevant experiments will use materials with this doping ratio for research.

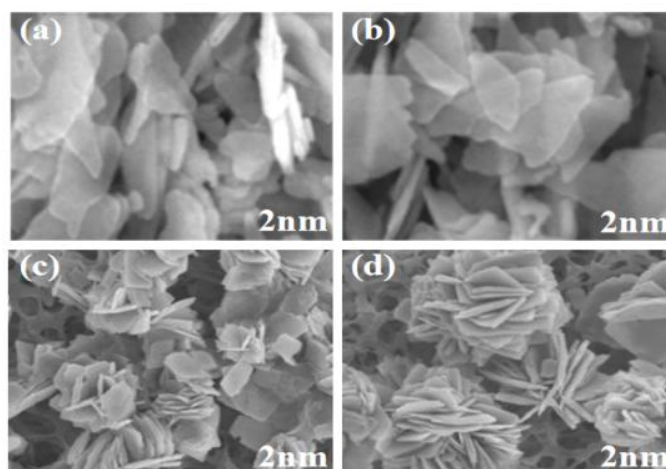


Figure 5. (a–d) Low-magnification SEM images of ZnFe<sub>2</sub>O<sub>4</sub>, 0.2% La-ZnFe<sub>2</sub>O<sub>4</sub>, 0.5% La-ZnFe<sub>2</sub>O<sub>4</sub> and 0.8% La-ZnFe<sub>2</sub>O<sub>4</sub> nanosheets.

We also analyzed the structure, crystallinity and phase of the material and conducted EDS (Energy Dispersive X-ray Spectroscopy) test analysis. As shown in (Figure 6f), the X-ray diffraction (XRD) pattern of La-ZnFe<sub>2</sub>O<sub>4</sub> was obtained using the X-ray diffractometer of Malvern Panalytical Ltd. An obvious peak appeared at  $2\theta = 29.077^\circ$ , proving that the La element was successfully doped. In order to further prove the prepared product La-ZnFe<sub>2</sub>O<sub>4</sub>, TEM elemental analysis test was also conducted, as shown in (Figure 6a–d). The test results show that there are four elements Zn, Fe, O and La, which once again shows that La has been successfully doped into ZnFe<sub>2</sub>O<sub>4</sub>.

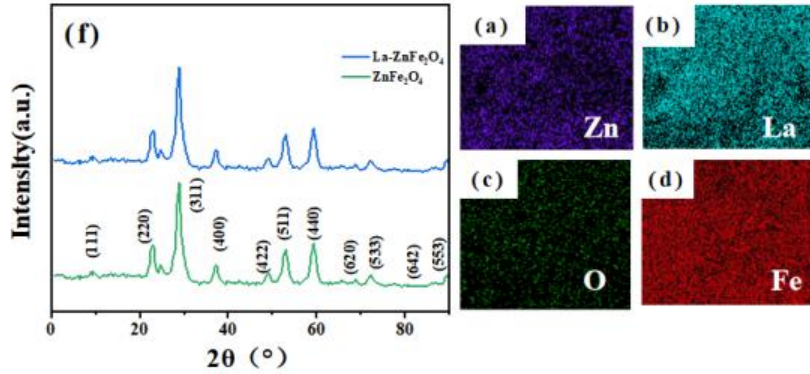


Figure 6. (a–d) TEM mapping of Zn, La, O and Fe elements; (f) XRD patterns of ZnFe<sub>2</sub>O<sub>4</sub> and La-ZnFe<sub>2</sub>O<sub>4</sub> nanosheets.

According to Wenzel's wetting theory, the interfacial wettability of hydrophilic materials is jointly controlled by surface roughness and water contact angle. When the droplet is in an environment without the action of an external force field, the surface tension causes it to assume a spherical outline; when the droplet contacts the solid surface, its final shape is determined by the relative size of the internal cohesion of the liquid and the adhesion force at the solid-liquid interface. The state in which the droplet spreads on the solid surface or forms a specific angle is defined as the contact angle. Wenzel's wetting equation can be expressed as  $\cos\theta_w = r\cos\theta$ , where  $r$  is the surface roughness ratio, that is, the ratio of the actual surface area of the material to the geometric projected surface area, and  $\theta$  is the intrinsic contact angle of an ideal smooth surface. Specifically, when the intrinsic contact angle  $\theta$  is less than  $90^\circ$ , the increase in surface roughness of the material will reduce the apparent contact angle  $\theta_w$ , and the lyophilicity of the material interface will be enhanced; when  $\theta$  is greater than  $90^\circ$ , the increase in roughness will cause  $\theta_w$  to increase, and the material will exhibit better lyophobic properties. It can be seen from the test results (Figure 7(1)–(5)) that the water contact angle of the CNTs material is  $0^\circ$ . This result shows that the CNTs material after acidification treatment has excellent hydrophilicity[20–22].

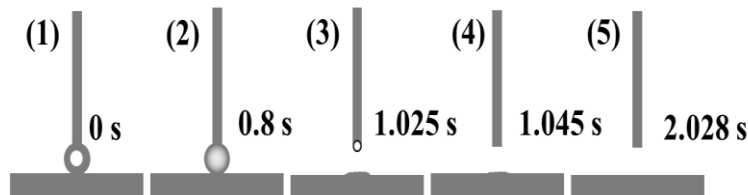


Figure 7. Water contact angle of CNTs materials.

To further verify the prepared hydrophilic carbon nanotubes, both pristine and hydrophilic carbon nanotubes were characterized by Fourier transform infrared (FTIR) spectroscopy. As shown in (Figure 8), it can be clearly seen that there are obvious troughs at  $1563\text{ cm}^{-1}$  and  $2745\text{ cm}^{-1}$ , which indicates that a large amount of  $\text{-COOH}$  appears in the hydrophilic carbon nanotubes we prepared. There is also an obvious trough at  $3421\text{ cm}^{-1}$ , which indicates that a large amount of  $\text{-OH}$  appears in the hydrophilic carbon nanotubes we prepared. Since  $\text{-COOH}$  and  $\text{-OH}$  are hydrophilic groups, the hydrophilicity of the carbon nanotubes we produced increased significantly, confirming that the previous hydrophilic carbon nanotubes were successfully prepared[23].

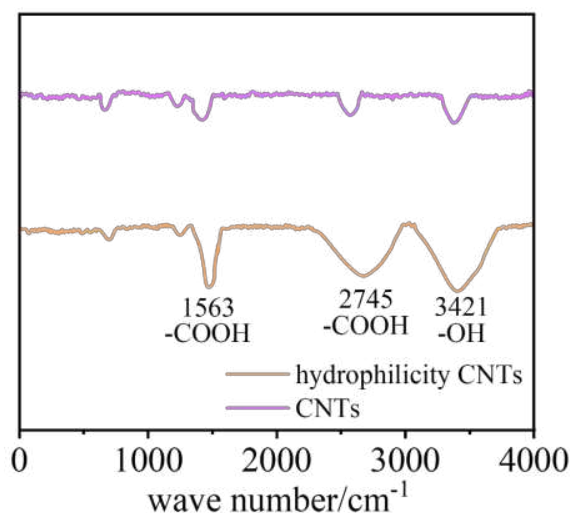


Figure 8. Fourier transform infrared (FTIR) spectrum of hydrophilic carbon nanotubes.

In order to verify the relevant conclusions in (Figure 6), this study used the nitrogen adsorption-desorption method to test the specific surface area (BET) and pore size distribution of  $\text{La-ZnFe}_2\text{O}_4$  and pure  $\text{ZnFe}_2\text{O}_4$ . The results are shown in (Figure 9). Figure 9a and b are the adsorption-desorption isotherms and pore size distribution curves of the four materials respectively. It can be seen from the isotherms that the four samples all show typical type IV isotherms, with high saturation adsorption pressure, gentle adsorption platform, and the slope increases significantly in the high relative pressure area; at the same time, their hysteresis loops are all H3 type, indicating that  $\text{ZnFe}_2\text{O}_4$  and  $\text{La-ZnFe}_2\text{O}_4$  are mesoporous materials. Unlike pure  $\text{ZnFe}_2\text{O}_4$ , which only has an obvious hysteresis loop in the relative pressure range of 0.8–1.0, 0.5%  $\text{La-ZnFe}_2\text{O}_4$  has a hysteresis loop at about 0.6, indicating that La doping is beneficial to the earlier formation of pores and increases the number of pores. According to the BET model calculation, the specific surface areas of  $\text{ZnFe}_2\text{O}_4$ , 0.2%  $\text{La-ZnFe}_2\text{O}_4$ , 0.5%  $\text{La-ZnFe}_2\text{O}_4$  and 0.8%  $\text{La-ZnFe}_2\text{O}_4$  are 67.2, 93.4, 114.8 and 99.2  $\text{m}^2/\text{g}$ , respectively. This value directly proves that La doping can significantly increase the specific surface area of  $\text{ZnFe}_2\text{O}_4$ , thereby providing more active sites for electrochemical reactions and accelerating the transport of electrolyte ions within the material. In terms of pore size distribution, the main peak pore diameters of the four materials are approximately 26, 29, 32 and 30 nm respectively, which further confirms the characteristics of the mesoporous structure; among them, 0.5%  $\text{La-ZnFe}_2\text{O}_4$  has an obvious characteristic peak at about 7 nm, indicating that the small pore content in this sample has significantly increased, which is beneficial to inhibiting excessive growth of grains and further increasing the specific surface area. To sum up, the increase in specific surface area and number of pores caused by La doping can provide sufficient active sites for electrode reactions, improve the material's infiltration and ion transport capabilities in the electrolyte, shorten the electron and ion

transport paths, and provide important structural support for the improvement of electrochemical performance.

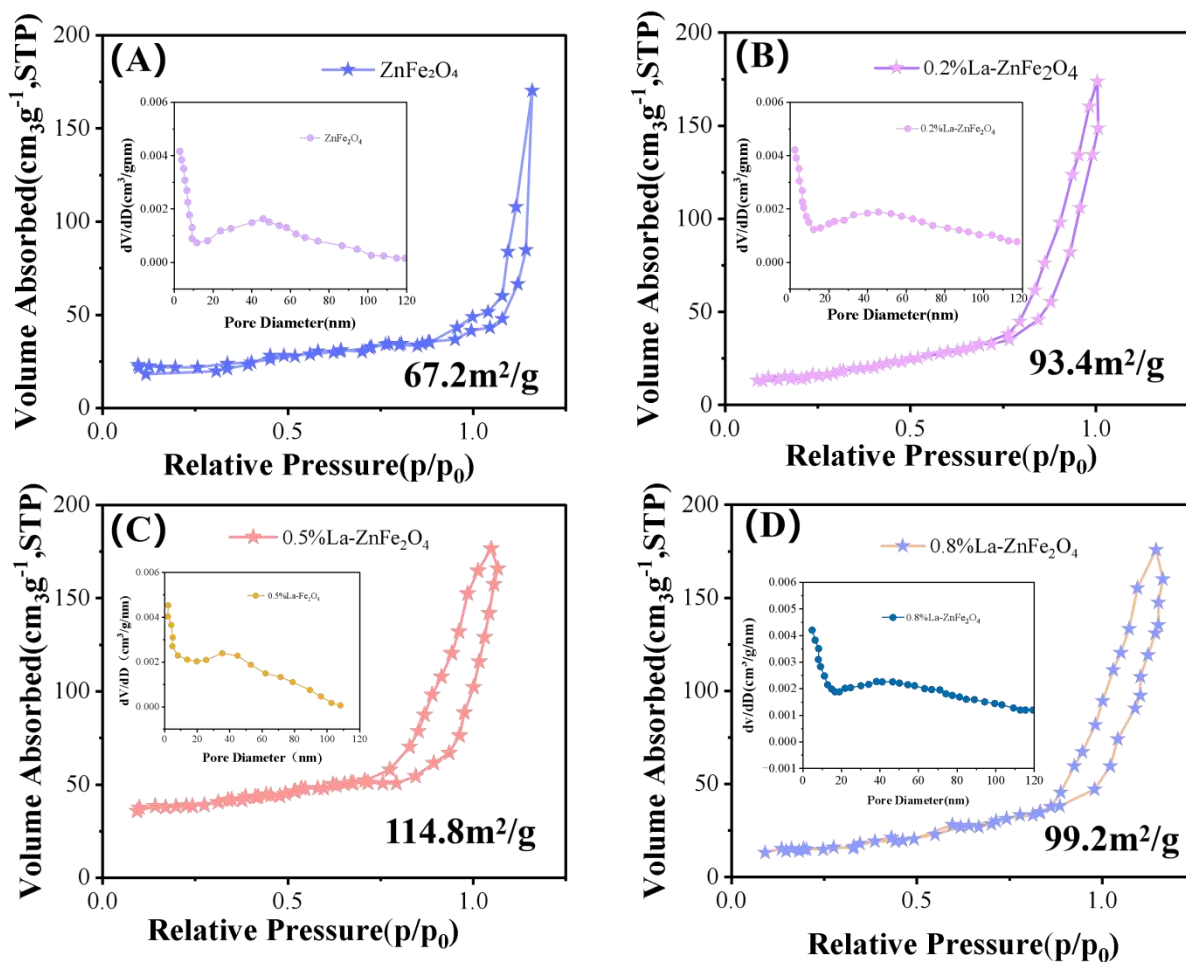


Figure 9. N<sub>2</sub> adsorption-desorption isotherms and pore size distribution of ZnFe<sub>2</sub>O<sub>4</sub>, 0.2% La-ZnFe<sub>2</sub>O<sub>4</sub>, 0.5% La-ZnFe<sub>2</sub>O<sub>4</sub> and 0.8% La-ZnFe<sub>2</sub>O<sub>4</sub>.

#### 4. Measurement of electrochemical properties of ZnFe<sub>2</sub>O<sub>4</sub> and La-ZnFe<sub>2</sub>O<sub>4</sub> nanosheet electrode materials

The electrochemical properties of the prepared electrode materials were tested in a three-electrode system with 2 M KOH as the electrolyte. A platinum sheet was used as the counter electrode, Hg/HgO was used as the reference electrode, and the prepared system material was used as the working electrode. Figure 10 shows the corresponding three-electrode system diagram[24].

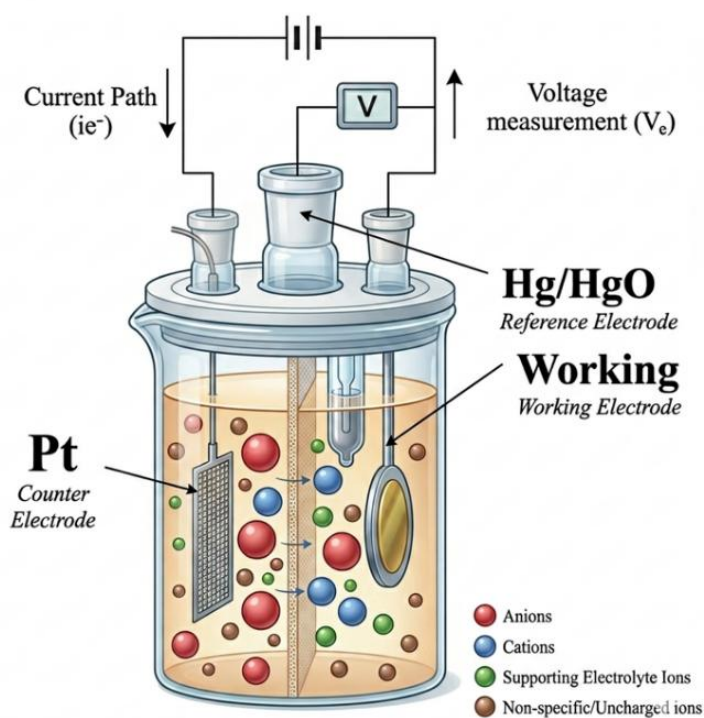


Figure 10. Three-electrode system diagram.

Figure 11 (a) shows the cyclic voltammetry (CV) curves of the same electrode material in four electrolytes: KOH, NaOH, LiOH and NaCl. All four curves show obvious redox peaks, indicating that the energy storage mechanism of the material is dominated by Faraday pseudocapacitance. Among them, the curve corresponding to KOH electrolyte has the largest integrated area and the highest redox peak current, followed by NaOH, while LiOH and NaCl, the curve area is significantly reduced and the peak current response is weak, which shows that the alkaline electrolyte is more conducive to the electrochemical reaction activity of the material, and KOH can provide the material with the most abundant electrochemical reaction sites and the largest charge storage capacity. At the same time, its peak shape is more symmetrical, which also reflects the better reversibility of the electrode reaction, while LiOH and NaCl will significantly limit the reaction kinetics of the material. On this basis, the galvanostatic charge-discharge (GCD) curve in (Figure 11b) further verifies the impact of the electrolyte on performance. All curves are asymmetric triangles, consistent with the CV results. Among them, the KOH electrolyte has the longest discharge platform and the smallest charge-discharge voltage difference, followed by NaOH. The discharge time of LiOH and NaCl is extremely short and quickly drops to the cut-off potential. This not only shows that KOH allows the material to release more charges, and also has smaller electrochemical polarization effects and higher energy conversion efficiency[25]. LiOH and NaCl will significantly reduce the material's capacity contribution and charge and discharge efficiency. Finally, the specific capacity histogram in (Figure 11c) at a current density of 3 A/g quantitatively summarizes the above results. KOH has the highest specific capacity (433 A·s/g), followed by NaOH (320 A·s/g), while NaCl (120 A·s/g) and LiOH (106 A·s/g) are much lower than the previous two. This result clarifies the performance ranking of this type of electrode materials in different electrolytes, revealing the key supporting role of alkaline electrolytes, especially KOH, in the energy storage performance of materials. The difference in electrolytes is mainly due to the cation radius and solvation effect. The moderate radius of  $K^+$  makes its migration resistance in the material lattice and pore channels minimal, while  $Li^+$  diffusion is hindered by strong solvation. This provides a direct experimental basis for the selection of

electrolyte for this type of electrode material. In actual device applications, KOH electrolyte should be preferred to achieve the best energy storage performance.

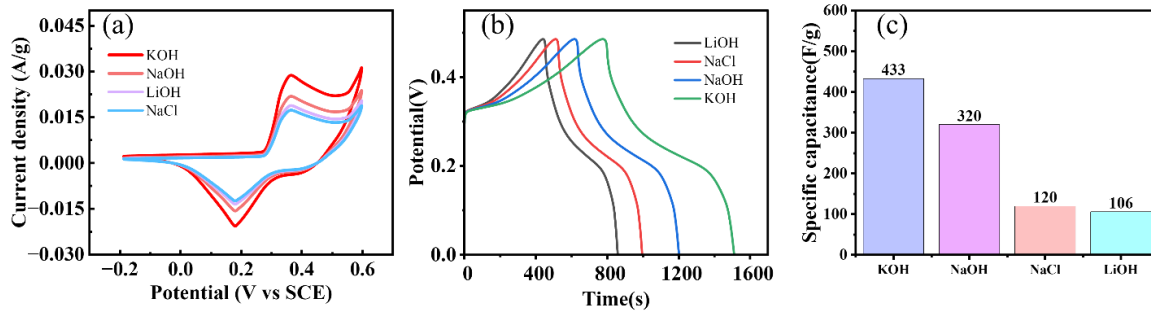


Figure 11. (a) Cyclic voltammetry (CV) curves of KOH, NaOH, LiOH and NaCl; (b) Galvanostatic charge-discharge (GCD) curves of KOH, NaOH, LiOH and NaCl; (c) Specific capacity diagram of KOH, NaOH, LiOH and NaCl at a current density of 3 A/g.

Figure 12 (a) shows the cyclic voltammetry (CV) curves of La-ZnFe<sub>2</sub>O<sub>4</sub> after annealing for 1, 9, 11 and 17 h. The curve shows an obvious redox peak, indicating that the energy storage mechanism of the material is dominated by Faraday pseudocapacitance. The larger area enclosed by the CV curve of the 11-hour annealed sample indicates that the specific capacitance is higher. This result directly affects the evaluation of the energy storage potential of the material and provides a key basis for subsequent optimization of annealing time. Figure 12 (b) presents the galvanostatic charge and discharge (GCD) curves of La-ZnFe<sub>2</sub>O<sub>4</sub> after annealing for 1, 9, 11 and 17 h. The charge and discharge times of the 11-hour and 17-hour samples are longer, reflecting higher specific capacitance and better reaction reversibility. This phenomenon affects the judgment of the rate performance and kinetics of the material, indicating that appropriately extending the annealing time can improve the ion transport and charge transfer process of the electrode. Figure 12 (c) is a histogram of the specific capacity of La-ZnFe<sub>2</sub>O<sub>4</sub> after annealing for 1, 9, 11 and 17 h at a current density of 3 A/g. The 11-hour annealed sample has the highest specific capacity (411 F/g). This data affects the understanding of the energy storage density of the material, indicating that moderate annealing can optimize the crystal structure and specific surface area, thereby increasing the specific capacity, providing quantitative support for selecting the optimal annealing process in practical applications. Figure 12 (d) Cycle performance diagram of La-ZnFe<sub>2</sub>O<sub>4</sub> nanosheets at a current density of 1 A/g. The capacity retention rate of the 11-hour annealed sample is significantly higher, and it can still maintain a high specific capacity after 8000 cycles[26]. This result affects the evaluation of the long-term stability of the material, indicating that optimizing the annealing time can enhance the stability of the electrode structure, reduce the capacity attenuation during cycling, and improve the service life of the device. Figure 12 (e) is the impedance diagram of La-ZnFe<sub>2</sub>O<sub>4</sub> after annealing for 1, 9, 11 and 17 h. The semicircle diameter in the high-frequency region of the Nyquist curve of the 11-hour sample is smaller and the slope in the low-frequency region is steeper, indicating that its charge transfer resistance and ion diffusion resistance are lower. This characteristic affects the understanding of the electrochemical kinetics of the material, indicating that appropriate annealing time can optimize the electrode interface structure, accelerate ion and electron transmission, thereby improving the overall electrochemical performance.

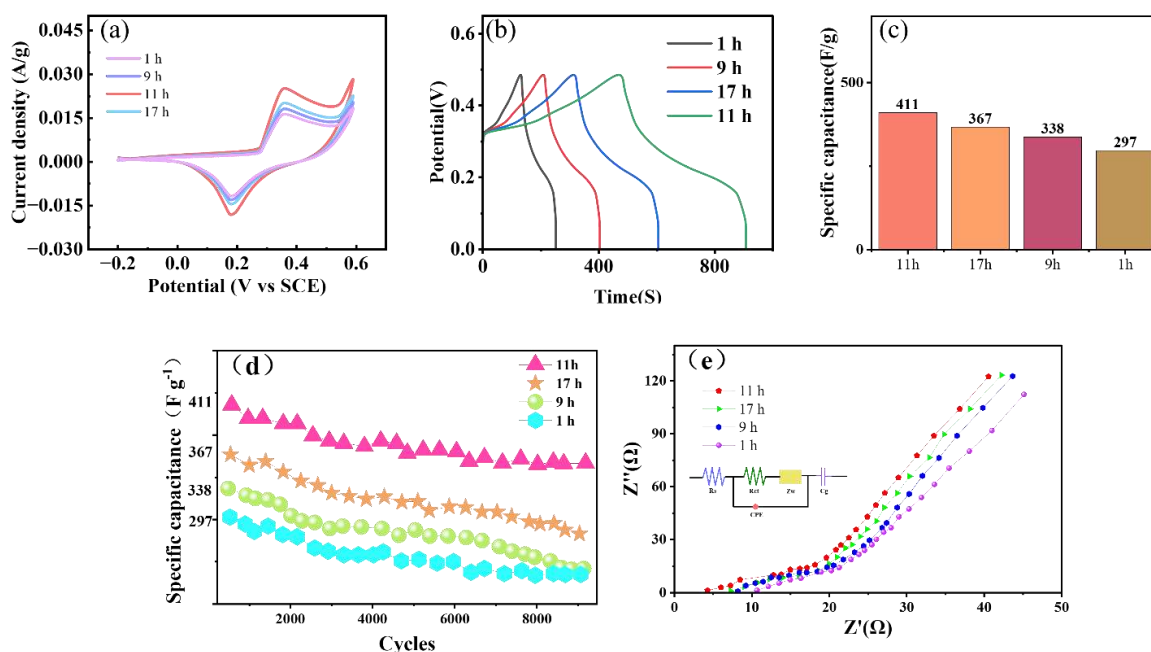


Figure 12. (a) Cyclic voltammetry (CV) curves of La-ZnFe<sub>2</sub>O<sub>4</sub> annealed for 1, 9, 11 and 17 h; (b) Galvanostatic charge-discharge (GCD) curves of La-ZnFe<sub>2</sub>O<sub>4</sub> annealed for 1, 9, 11 and 17 h; (c) Specific capacity diagram of La-ZnFe<sub>2</sub>O<sub>4</sub> annealed for 1, 9, 11 and 17 h at a current density of 3 A/g; (d) Cycle performance diagram of La-ZnFe<sub>2</sub>O<sub>4</sub> nanosheet electrode at a current density of 1 A/g; (e) Impedance diagram of La-ZnFe<sub>2</sub>O<sub>4</sub> annealed for 1, 9, 11 and 17 h.

Figure 13 (a) is the cyclic voltammetry (CV) curve of ZnFe<sub>2</sub>O<sub>4</sub>, 0.2% La-ZnFe<sub>2</sub>O<sub>4</sub>, 0.5% La-ZnFe<sub>2</sub>O<sub>4</sub> and 0.8% La-ZnFe<sub>2</sub>O<sub>4</sub> at 4 mV/s. All samples have obvious redox peaks in the 0.2–0.5 V range, of which 0.5% La-ZnFe<sub>2</sub>O<sub>4</sub> has the largest current density and the most prominent peak shape, while undoped ZnFe<sub>2</sub>O<sub>4</sub> has the weakest current response. This shows that an appropriate amount of La doping can significantly improve the electrochemical activity and charge transfer capability of the material, while excessive doping (0.8%) will cause a slight drop in performance. This result provides a direct basis for optimizing the La doping ratio, and also shows that 0.5% is an ideal doping concentration in this system, which is conducive to giving full play to the pseudocapacitive effect, and also provides an experimental basis for subsequent kinetic analysis and material design. Figure 13 (b) is the galvanostatic charge-discharge (GCD) curve of the above four materials at 4 mV/s. The curve shows obvious nonlinear characteristics, which is consistent with the CV results, confirming the dominant role of pseudocapacitance. Among them, 0.5% La-ZnFe<sub>2</sub>O<sub>4</sub> has the longest discharge time, followed by 0.2% La-ZnFe<sub>2</sub>O<sub>4</sub>, while undoped ZnFe<sub>2</sub>O<sub>4</sub> has the shortest discharge time. This shows that an appropriate amount of La doping can effectively extend the charge and discharge time and improve the charge storage capacity. It also verifies the conclusion of the CV curve, provides visual evidence for evaluating the energy storage capacity under different doping ratios, and also provides experimental support for optimizing charge and discharge strategies and improving energy utilization efficiency[27]. Figure 13 (c) is a histogram of the specific capacity of the four materials when the current density is 3 A/g. The specific data are: 0.8% La-ZnFe<sub>2</sub>O<sub>4</sub> is 362 F/g, 0.5% La-ZnFe<sub>2</sub>O<sub>4</sub> is 426 F/g, and 0.2% La-ZnFe<sub>2</sub>O<sub>4</sub> is 263 F/g, undoped ZnFe<sub>2</sub>O<sub>4</sub> is 186 F/g. This data directly quantifies the impact of different doping ratios on the specific capacity of the material. 0.5% La-ZnFe<sub>2</sub>O<sub>4</sub> exhibits the highest specific capacity, significantly better than other samples. This not only verifies the positive effect of appropriate La doping on improving energy storage performance,

but also provides key performance parameters for the practical application of this material in supercapacitors, while highlighting the potential of 0.5% La-ZnFe<sub>2</sub>O<sub>4</sub> as a high-performance electrode material and provides a quantitative basis for subsequent device design and performance optimization. Taken together, this set of figures systematically reveals the regulation effect of La doping ratio on ZnFe<sub>2</sub>O<sub>4</sub> electrode performance from the three dimensions of electrochemical behavior, charge and discharge characteristics and specific capacity. It not only clarifies that 0.5% is the optimal doping concentration, but also provides experimental basis for understanding the impact mechanism of doping modification on the energy storage performance of transition metal oxides, laying the foundation for the subsequent development of higher-performance supercapacitor electrode materials.

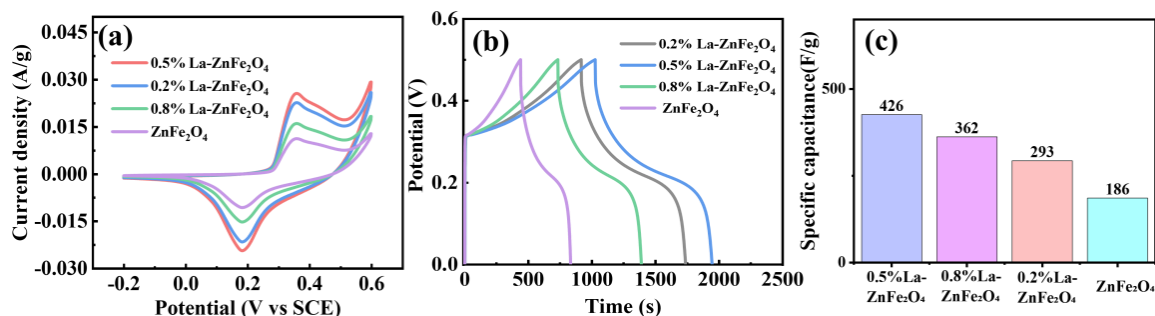


Figure 13. (a) Cyclic voltammetry (CV) curves of ZnFe<sub>2</sub>O<sub>4</sub>, 0.2% La-ZnFe<sub>2</sub>O<sub>4</sub>, 0.5% La-ZnFe<sub>2</sub>O<sub>4</sub> and 0.8% La-ZnFe<sub>2</sub>O<sub>4</sub>; (b) Galvanostatic charge-discharge (GCD) curves of ZnFe<sub>2</sub>O<sub>4</sub>, 0.2% La-ZnFe<sub>2</sub>O<sub>4</sub>, 0.5% La-ZnFe<sub>2</sub>O<sub>4</sub> and 0.8% La-ZnFe<sub>2</sub>O<sub>4</sub> at 4 mV/s; (c) Specific capacity diagram of ZnFe<sub>2</sub>O<sub>4</sub>, 0.2% La-ZnFe<sub>2</sub>O<sub>4</sub>, 0.5% La-ZnFe<sub>2</sub>O<sub>4</sub> and 0.8% La-ZnFe<sub>2</sub>O<sub>4</sub> at a current density of 3 A/g.

Figure 14 (a) is the cyclic voltammetry (CV) curve of La-ZnFe<sub>2</sub>O<sub>4</sub> at different scan rates of 10–100 mV/s. The curve shows an obvious redox peak in the 0.2–0.5 V range, and as the scan rate increases, the peak position shifts slightly but the shape remains good. This shows that the material can still maintain an efficient charge transfer reaction under fast scan, reflecting good rate response capability, which provides a basis for its application in fast charge and discharge scenarios. It also shows that the electrochemical active sites of La-ZnFe<sub>2</sub>O<sub>4</sub> can still effectively participate in the reaction at high scan rates, providing a direct basis for subsequent kinetic analysis. Figure 14 (b) Charge-discharge curves of La-ZnFe<sub>2</sub>O<sub>4</sub> nanosheets at different scan rates of 10–100 mV/s. The curve shows obvious nonlinear characteristics, which is consistent with the CV results, confirming the dominant role of pseudocapacitance, and the discharge time is significantly longer at low current density, indicating that the active sites are more fully utilized at this time. This result not only verifies the capacitance mechanism of the material, but also provides experimental support for optimizing the charge and discharge strategy and improving energy utilization efficiency. At the same time, the nonlinear charge and discharge curve further supports the Faradaic reaction characteristics of the material, and provides visual evidence for distinguishing the contribution of double layer capacitance and pseudocapacitance. Figure 14 (c) is a histogram of specific capacitance at different scan rates, which quantifies the rate performance of the electrode: the specific capacitance is as high as 422 F/g at 100 mV/s, 372 F/g at 80 mV/s, 327 F/g at 60 mV/s, 271 F/g at 20 mV/s, and remains 242 F/g at 10 mV/s. This data intuitively reflects the charge storage capability of the material at high rates, proves that it can still output stably in high-power application scenarios, and provides key performance parameters for actual device design. At the same time, the ultra-high specific capacitance also highlights the energy storage potential of La-ZnFe<sub>2</sub>O<sub>4</sub> nanosheets as electrode materials, laying a quantitative foundation for its application in the field of supercapacitors. Figure 14 (d) is a linear plot of

logarithmic current ( $\log i$ ) versus logarithmic scan rate ( $\log v$ ). The slopes of the anodic and cathodic processes are 0.83 and 0.77, respectively, both close to 1, which indicates that the electrode process is dominated by surface-controlled pseudocapacitive reactions rather than diffusion control. This dynamic characteristic means that charge storage mainly occurs on the surface of the material, which is conducive to rapid charge and discharge, further supporting the excellent rate performance of the material, and also providing theoretical guidance for regulating the material structure to strengthen surface reactions and improve rate performance. Figure 14 (e) is a histogram of pseudocapacitance contribution rates at different scan rates. As the scan rate increases from 2 mV/s to 20 mV/s, the pseudocapacitance contribution increases from 43% at 2 mV/s to 68% at 20 mV/s, which shows that under fast charge and discharge conditions, surface-controlled pseudocapacitance becomes the dominant mechanism for charge storage, while the contribution of diffusion control is suppressed. This result reveals the capacitance behavior transformation of the material under different working conditions, and provides a dynamic explanation for understanding its rate performance [28].

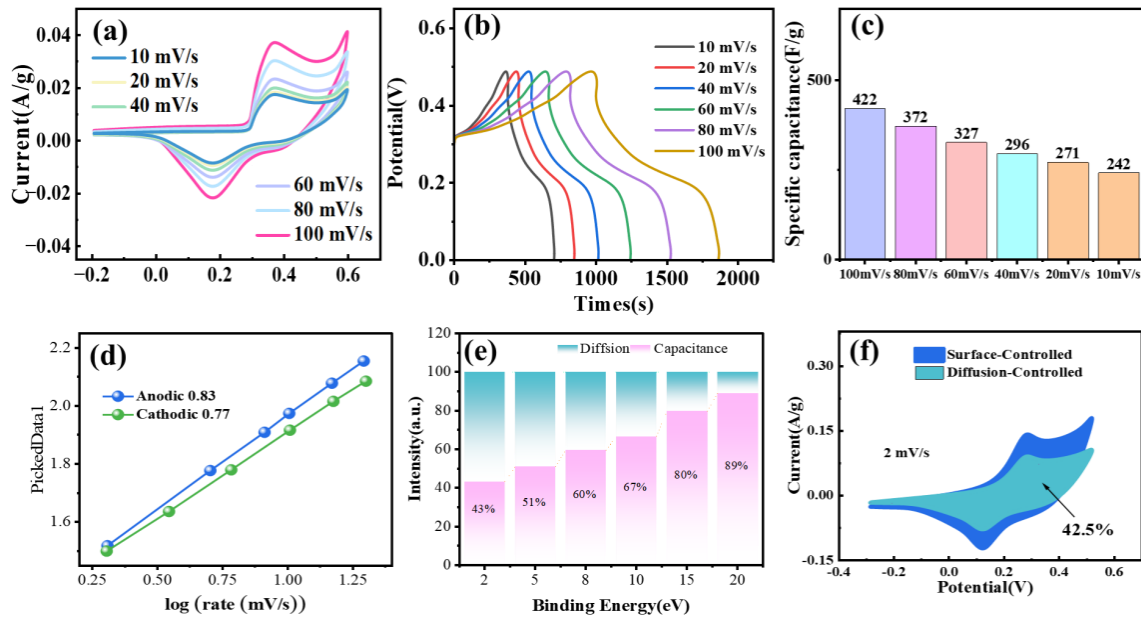


Figure 14. (a) Cyclic voltammetry (CV) curves of La-ZnFe<sub>2</sub>O<sub>4</sub> at different scan rates; (b) Charge-discharge curves of La-ZnFe<sub>2</sub>O<sub>4</sub> nanosheets at different scan rates; (c) Specific capacity of La-ZnFe<sub>2</sub>O<sub>4</sub> nanosheets at different scan rates; (d) Linear plot of  $\log(i)$  versus  $\log(v)$ ; (e) Contribution rate of pseudocapacitance at different scan rates; (f) Current at 10 mV/s divided into surface-controlled and diffusion-controlled contributions.

Figure 15 shows the rate and cycle performance of the La-ZnFe<sub>2</sub>O<sub>4</sub> nanosheet electrode under different current densities. The abscissa is the number of charge and discharge cycles (0–600 times), and the ordinate is the specific capacitance. The different platforms in the figure correspond to 8 A/g, 3 A/g, 10 A/g, 1 A/g, 5 A/g, 10 A/g, 8 A/g. Specific capacitance performance under different current densities: initially the specific capacitance is about 302 F/g at 8 A/g, increases to about 354 F/g after switching to 3 A/g, drops back to about 271 F/g at 10 A/g, and reaches a peak of about 421 F/g at 1 A/g, then switches to 5 A/g, then 10 A/g and finally 8 A/g, the specific capacitance is stable at about 323 F/g, 262 F/g and 304 F/g respectively, and the specific capacitance can maintain a stable platform at each current density, and can return to the initial level when switching back to the same current density without obvious attenuation. This result shows that the La-ZnFe<sub>2</sub>O<sub>4</sub> nanosheet electrode not only exhibits an ultra-high specific capacitance of about 421 F/g at 1 A/g, but also maintains a specific capacitance of about 271 F/g even at a high current density of 10 A/g, demonstrating excellent rate performance and suitable for high-power applications with fast charge and discharge; at the same time, after 600 cycles and multiple current density switches, the specific capacitance has no significant attenuation, proving that the material structure remains stable during long-term charge and discharge processes, the active material is not easily lost or the structure collapses, and it has outstanding cycle stability. This synergistic performance of high specific capacitance, excellent rate performance and cycle stability makes La-ZnFe<sub>2</sub>O<sub>4</sub> nanosheets a strong candidate for supercapacitor electrode materials. It has important application value especially in fields such as electric vehicles and smart grid energy storage that take into account high energy density and high power density[29]. It also verifies the effectiveness of La doping and nanosheet structural design, and provides experimental basis and design ideas for the subsequent development of higher performance transition metal oxide electrode materials.

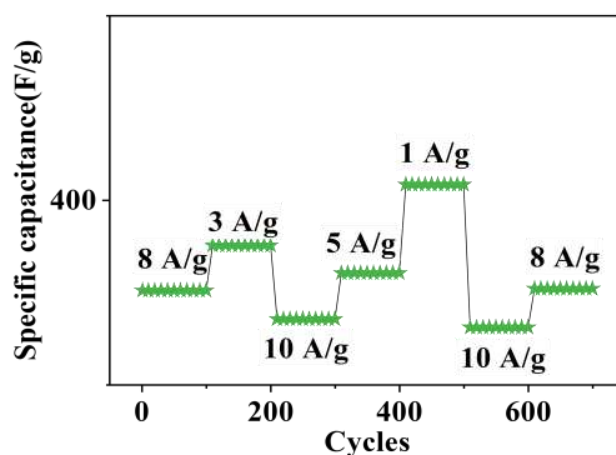


Figure 15. Rate and cycle performance of La-ZnFe<sub>2</sub>O<sub>4</sub> nanosheets at different current densities.

## 5. Overview of performance analysis of asymmetric supercapacitor devices

In order to further explore the chemical properties of La-ZnFe<sub>2</sub>O<sub>4</sub>, this study constructed an asymmetric supercapacitor using La-ZnFe<sub>2</sub>O<sub>4</sub> composite material as the positive electrode and carbon nanotubes as the negative electrode. The specific preparation process is as follows: first prepare the positive electrode, mix La-ZnFe<sub>2</sub>O<sub>4</sub>, conductive carbon black and polyvinylidene fluoride at a mass ratio of 5:1:1, add the solvent drop by drop and stir evenly, then coat it on the carbon cloth, dry it under vacuum conditions at 100 °C for 10 h to obtain a positive electrode with an area of 1 cm<sup>2</sup>; use the same ratio for the negative electrode, mix hydrophilic carbon nanotubes, conductive carbon black

and polyvinylidene fluoride and coat it on the carbon cloth, and use the same drying process to make a negative electrode with an area of 1 cm<sup>2</sup>; after the electrode shell is ultrasonically cleaned with ethanol and dried, the device assembly begins: place the negative electrode sheet in sequence in the negative electrode shell and add a small amount of PVA-KOH electrolyte, lay a moistened polypropylene separator, then insert the positive electrode sheet and add electrolyte dropwise, and then stack the gasket, shrapnel and positive electrode shell. After being pressed by a tablet press, solidify at 25 °C and vacuum dry for 20 h to finally complete the device preparation. For the specific structure of the supercapacitor, please refer to (Figure 16)

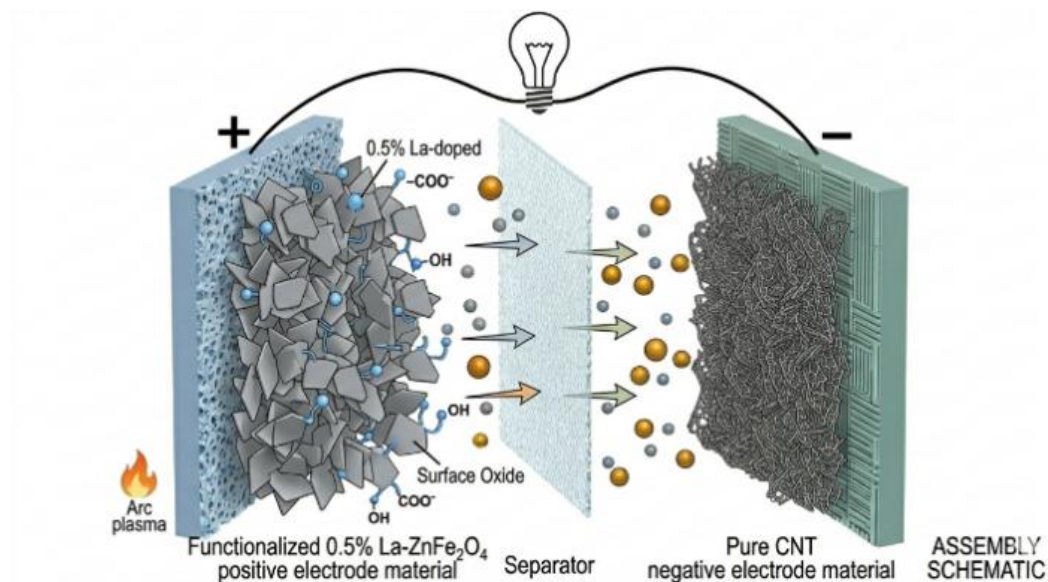


Figure 16. Schematic diagram of the working principle of the supercapacitor device.

Figure 17 (a) is the cyclic voltammogram (CV) curve of pure CNTs and La-ZnFe<sub>2</sub>O<sub>4</sub>, with a scan rate of 10 mV/s. The curve of pure CNTs is approximately rectangular, showing typical double-layer capacitance behavior, while the curve of La-ZnFe<sub>2</sub>O<sub>4</sub> has an obvious redox peak, and the current density is much larger than that of CNTs, which indicates that the capacitance contribution of La-ZnFe<sub>2</sub>O<sub>4</sub> mainly comes from Faraday pseudocapacitance, and its electrochemical activity is significantly higher than that of pure CNTs. This result directly proves that La-ZnFe<sub>2</sub>O<sub>4</sub> as an active material can effectively improve the charge storage capacity of the electrode and provides a core basis for the design of composite materials. Figure 17 (b) shows the CV curves of La-ZnFe<sub>2</sub>O<sub>4</sub>/CNTs electrode under different voltage windows (0–0.8 V to 0–1.8 V). As the voltage window expands, the redox peak of the curve becomes clearer and the current response is enhanced, which indicates that the Faradaic reaction of the electrode material can proceed more fully within a wider potential range, broadening the operating voltage range of the electrode. The wider voltage window means that the supercapacitor can operate at a higher energy density, which is of great significance to improving the overall energy storage performance of the device. Figure 17 (c) presents the CV curves of La-ZnFe<sub>2</sub>O<sub>4</sub>/CNTs electrode at different scan rates (10–100 mV/s). Even if the scan rate is increased to 100 mV/s, the curve still maintains a good shape and the redox peak is still clearly discernible, which shows that the electrode material has excellent rate performance and can still maintain an efficient electrochemical response during fast charge and discharge. This excellent rate performance makes the material have significant application advantages in scenarios that require fast charge and discharge (such as electric vehicles, portable electronic devices). Figure 17 (d) shows the galvanostatic charge-discharge (GCD) curves of La-ZnFe<sub>2</sub>O<sub>4</sub>/CNTs electrode at different current densities (0.5–10 A/g). The curve shows obvious nonlinear characteristics, which is consistent with

the CV results, further confirming the dominant role of pseudocapacitance; at the same time, at a low current density of 0.5 A/g, the discharge time is significantly prolonged, indicating that the active sites of the electrode material are more fully utilized at this time. This result not only verifies the capacitance mechanism of the material, but also provides experimental support for optimizing charge and discharge strategies and improving energy utilization efficiency. Figure 17 (e) is a histogram of specific capacitance at different current densities, which quantifies the rate performance of the electrode: the specific capacitance is 162 F/g at 0.5 A/g, 141 F/g at 5 A/g, 128 F/g at 10 A/g, 92 F/g at 15 A/g, and 78 F/g at 20 A/g. As the current density increases, although the specific capacitance decreases, it still maintains about 48% of the initial capacitance at 20 A/g. This data intuitively reflects the charge storage capability of the material at high rates, proves that it can still output stably in high-power application scenarios, and provides practical guidance for device design.

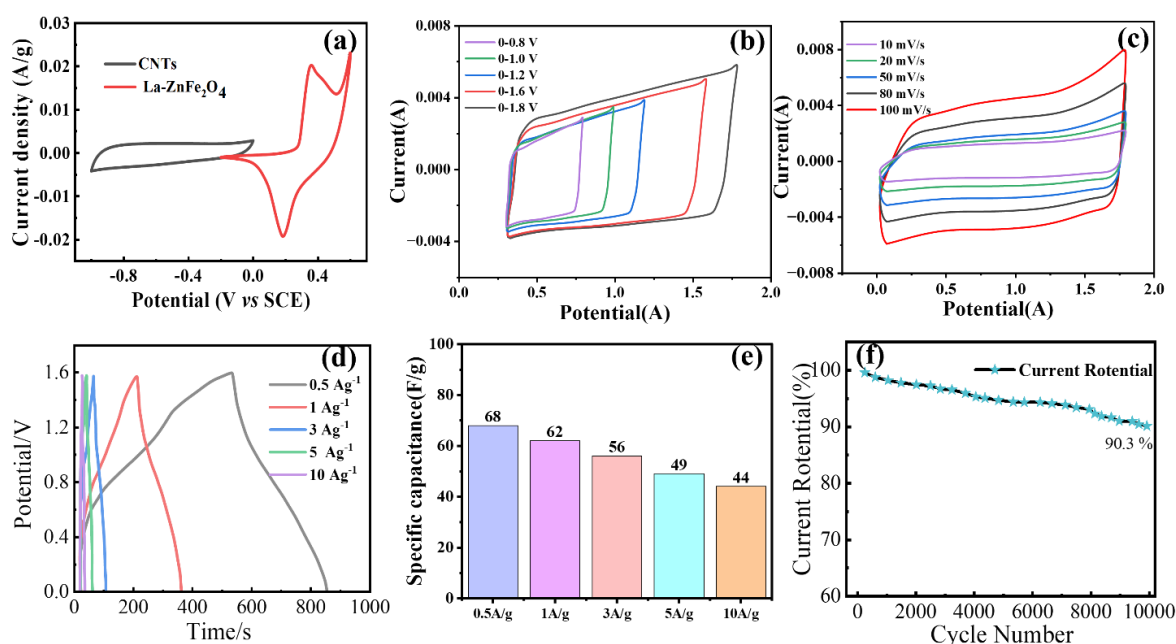


Figure 17. (a) Cyclic voltammetry (CV) curves of La-ZnFe<sub>2</sub>O<sub>4</sub>//CNTs electrode and CNTs in a three-electrode cell with 2 M KOH electrolyte at a scan rate of 10 mV/s; (b) Cyclic voltammetry curves of La-ZnFe<sub>2</sub>O<sub>4</sub>//CNTs at different scan rates; (c) Charging of La-ZnFe<sub>2</sub>O<sub>4</sub>//CNTs electrode at different current densities; (d) Charge and discharge curves at different potentials when the current density is 4 A/g; (e) Specific capacity diagram of La-ZnFe<sub>2</sub>O<sub>4</sub>//CNTs at different scan rates; (f) Cyclic stability performance of the La-ZnFe<sub>2</sub>O<sub>4</sub>//CNTs device when the current density is 10 A/g.

Figure 18 shows that compared with other similar devices, this device has better energy density and power density. This advantage is also due to the synergistic effect of the positive and negative materials of the device, which effectively balances the performance requirements of energy storage and power output[22].

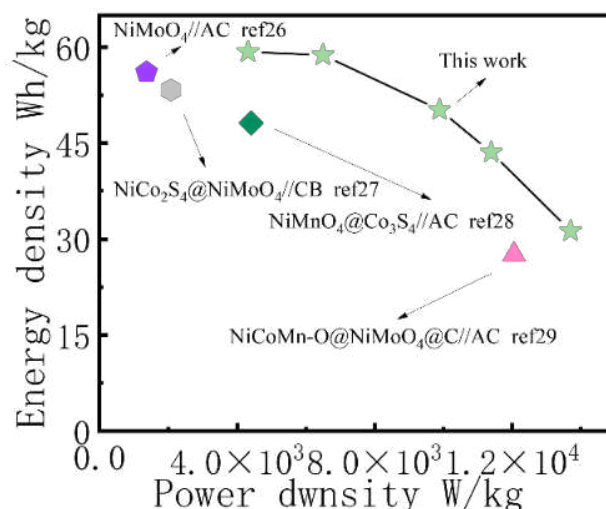


Figure 18. Ragone plot of power density and energy density of La-ZnFe<sub>2</sub>O<sub>4</sub>//CNTs devices compared with other energy storage devices.

## 6. Conclusion

This study successfully prepared a high-performance porous sheet-like La-ZnFe<sub>2</sub>O<sub>4</sub> cathode material through La doping modification, and combined it with a hydrophilic carbon nanotube anode prepared by acid-base modification to construct an asymmetric supercapacitor with both high energy density and high power density, effectively solving the core problem of low energy density of traditional supercapacitors. Experiments have determined that 12 h is the optimal doping reaction time for La-ZnFe<sub>2</sub>O<sub>4</sub> and 0.5% is the optimal La doping ratio. The material prepared under these conditions exhibits a high specific surface area of 114.8 m<sup>2</sup>/g and an ultra-high specific capacity of 426 F/g. It has, and the energy storage mechanism is mainly surface-controlled pseudocapacitance. The pseudocapacitance contribution rate can reach 68% at high scan rates, and it has excellent rate performance and cycle stability. The assembled La-ZnFe<sub>2</sub>O<sub>4</sub>//hydrophilic carbon nanotube asymmetric supercapacitor still has a capacitance retention rate of 83.2% after 10,000 cycles at a current density of 10 A/g. The energy density and power density are superior to most similar energy storage devices, which fully reflects the synergistic advantages of the structure and performance of the positive and negative electrode materials. This research provides an experimental reference for the modification design of rare earth-doped transition metal oxides, and also opens up a new path for the development of high-performance supercapacitor electrode materials. The prepared electrode materials and asymmetric devices have good practical application prospects in the fields of electrochemical energy storage such as portable electronic equipment, new energy vehicles, and smart grids. In the future, the electronic conduction and ion diffusion properties of the material can be further optimized through multi-element doping, composite modification, etc., while the large-scale preparation process of the device can be explored to promote its transition from laboratory research to industrial application.

## Authorship contribution statement

**Pengxiang Ma:** Manuscript writing, preparation and characterization of experimental materials, sorting of experimental data. **Jinshan Cao:** Drawing of preparation flow chart, sorting of experimental data. **Yongnan Tan:** Electrochemical performance analysis of electrode materials, construction of

three-electrode test system. **Meiyue Wu:** Sorting and analysis of experimental data. **Kunxi Li:** Sorting of experimental data. **Jingting Sun:** Hydrophilicity test of carbon nanotubes. **Jing Wang:** Funding acquisition. All authors participated in the revision of the manuscript, read and approved the final version of the manuscript.

## Declaration of Competing Interest

The authors declare no competing interests.

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## Data availability

The data presented in this study are available in this article.

## References

- [1] Wu, C.; Wang, X.; Liu, L. Editorial: Energy, economy, and climate interactions: challenges and opportunities. *Front. Earth Sci.* 2023, 11, 1298407. DOI: 10.3389/feart.2023.1298407.
- [2] Yu, K.; Sung, J.; Zhou, Y. Data governance in the geopolitics of energy transition: comparing regional energy cooperation in ASEAN and the EU. *Polit. Gov.* 2025, 13, 10429. DOI: 10.17645/pag.10429.
- [3] Babu, I. M.; Rathinamala, I. Fabrication of high-performance asymmetric supercapacitor utilizing tin oxide nanorods and carbon-based electrodes. *J. Electron. Mater.* 2024, 53, 547–556. DOI: 10.1007/s11664-023-10803-1.
- [4] Kim, S. C.; Choi, S. Q.; Park, J. Asymmetric supercapacitors using porous carbons and iron oxide electrodes derived from a single Fe metal-organic framework (MIL-100(Fe)). *Nanomaterials* 2023, 13, 1824. DOI: 10.3390/nano13121824.
- [5] Alharbi, A. Boosting supercapacitor performance through innovative transition metal-based electrode materials. *RSC Adv.* 2025, 15, 34551–34582. DOI: 10.1039/D5RA02905H.
- [6] Raikwar, A. S.; Panda, H. S. A review on nano-structured electrodes for high-performance supercapacitors: panoramic insights across dimensional spectra. *Discover Electron.* 2025, 2, 94. DOI: 10.1007/s44291-025-00132-4.

- [7] Li, X.; Xiong, S.; Li, G.; Xiao, S.; Zhang, C.; Ma, Y. Effect of microstructure on electrochemical performance of electrode materials for microsupercapacitor. *Mater. Lett.* 2023, 346, 134481. DOI: 10.1016/j.matlet.2023.134481.
- [8] Girirajan, M.; Bojarajan, A. K.; Pulidindi, I. N.; Hui, K. N.; Sangaraju, S. An insight into the nanoarchitecture of electrode materials on the performance of supercapacitors. *Coord. Chem. Rev.* 2024, 518, 216080. DOI: 10.1016/j.ccr.2024.216080.
- [9] Bhanuse, G. B.; Kumar, S.; Yu, C.-C.; Fu, Y.-P. Nanostructured  $\text{ZnCo}_2\text{O}_4@\text{NiMn-LDH}$  electrodes for supercapacitor and zinc-air battery application. *ACS Appl. Nano Mater.* 2024, 7, 13649–13663. DOI: 10.1021/acsanm.4c02138.
- [10] Sun, Y.; Niu, X.; Yang, L.; Mi, N.; Zhao, L. Controllable nitrogen-doped carbon nano-hollow cage structures as supercapacitor electrode materials. *Preprints.org* 2025. DOI: 10.20944/preprints202504.0339.v1.
- [11] Wang, L.; Li, B.; Bai, H.; Ding, H.; Xu, N.; Yin, C.; Xiong, J.; Yang, Z.; Rao, X.; Dong, B. Preparation of nitrogen-doped  $\text{ZnFe}_2\text{O}_4$ -modified carbon composite and its collaborative energy storage mechanism. *Coatings* 2023, 13, 1126. DOI: 10.3390/coatings13061126.
- [12] Zeng, X.; Liu, J.; Chu, K.; He, J.; Zhang, J.; Zhu, H.; Peng, Y. Atomic-level cation occupation and magnetic properties of  $\text{Ce}^{3+}$ -doped  $\text{ZnFe}_2\text{O}_4$  spinel ferrite. *RSC Adv.* 2025, 15, 20908–20915. DOI: 10.1039/D5RA01515D.
- [13] Qin, H.; Xiao, L.; Hao, J.; Wang, Y.; Huang, J.; Yang, G.; Xing, B. Rare earth doping: a strategy to enhance the catalytic activity of  $\text{ZnFe}_2\text{O}_4$  in activating peroxymonosulfate for acetaminophen degradation. *RSC Adv.* 2025, 15, 28651–28658. DOI: 10.1039/D5RA05044H.
- [14] Shi, F.; Xing, B.; Zeng, H.; Yuan, S.; Meng, W.; Qu, X.; Huang, G.; Zhang, C.; Chen, Z.; Jiao, L. Porous carbon nanorods induced by electrostatically assembling carbon quantum dots within the confined hollow space of halloysite for lithium-ion battery anodes. *Adv. Funct. Mater.* 2025, 35, 2501751. DOI: 10.1002/adfm.202501751.
- [15] Tong, Z.; Lv, C.; Bai, G.-D.; Yin, Z.-W.; Zhou, Y.; Li, J.-T. A review on applications and challenges of carbon nanotubes in lithium-ion battery. *Carbon Energy* 2025, 7, e643. DOI: 10.1002/cey2.643.
- [16] Liu, Y.; Sahoo, G.; Kim, E. M.; Jeong, S. M. Copper-iron selenides nanoflakes and carbon nanotubes composites as an advanced anode material for high-performance lithium-ion batteries. *Adv. Energy Sustain. Res.* 2024, 5, 2300234. DOI: 10.1002/aesr.202300234.
- [17] Zhao, X.; Wang, M.; Yue, S.; Wu, Y.; Zhang, Y.; Dong, Y.; Ma, T.  $\text{Fe}_7\text{S}_8$  nanoparticles embedded in sulfur-nitrogen codoped carbon nanotubes: a high-performance anode material for lithium-ion batteries with

- multilevel confinement structure. *ChemElectroChem* 2025, 12, e202500066. DOI: 10.1002/celec.202500066.
- [18] Jia, Z.; Qin, G.; Li, A.; Hu, K.; Wu, H.; Jin, G.; Zhu, J.; Chen, J. Waxberry-like TiO<sub>2</sub> with synergistic surface modification of pyrolytic carbon coating and carbon nanotubes as an anode for Li-ion battery. *Langmuir* 2024, 40, 24540–24549. DOI: 10.1021/acs.langmuir.4c03324.
- [19] Volkov, F. S.; Kamenskii, M. A.; Tolstopjatova, E. G.; Voskanyan, L. A.; Bobrysheva, N. P.; Osmolovskaya, O. M.; Eliseeva, S. N. Synthesis of ZnFe<sub>2</sub>O<sub>4</sub> nanospheres with tunable morphology for lithium storage. *Nanomaterials* 2023, 13, 3126. DOI: 10.3390/nano13243126.
- [20] Razavifar, M.; Abdi, A.; Nikooee, E.; Aghili, O.; Riazi, M. Quantifying the impact of surface roughness on contact angle dynamics under varying conditions. *Sci. Rep.* 2025, 15, 16611. DOI: 10.1038/s41598-025-01127-7.
- [21] Ma, Q.; Yang, Q.; Zhang, J.; Ren, F.; Xia, C.; Chen, F. Anti-corrosion properties of bio-inspired surfaces: a systematic review of recent research developments. *Mater. Adv.* 2024, 5, 2689–2718. DOI: 10.1039/D3MA01058A.
- [22] Barthwal, S.; Uniyal, S.; Barthwal, S. Nature-inspired superhydrophobic coating materials: drawing inspiration from nature for enhanced functionality. *Micromachines* 2024, 15, 391. DOI: 10.3390/mi15030391.
- [23] Wang, J.; Li, Y.; Zhao, Y.; Zhang, D.; Song, S.; Ke, J. Synthesis of NiCo<sub>2</sub>S<sub>4</sub>@NiMoO<sub>4</sub> nanosheets with excellent electrochemical performance for supercapacitor. *Crystals* 2022, 12, 821. DOI: 10.3390/cryst12060821.
- [24] Tang, X.; Lui, Y. H.; Zhang, B.; Hu, S. Venus flytrap-like hierarchical NiCoMn–O@NiMoO<sub>4</sub>@C nanosheet arrays as free-standing core-shell electrode material for hybrid supercapacitor with high electrochemical performance. *J. Power Sources* 2020, 477, 228977. DOI: 10.1016/j.jpowsour.2020.228977.
- [25] Barthwal, Subodh, Surbhi Uniyal, and Sumit Barthwal. "Nature-inspired superhydrophobic coating materials: drawing inspiration from nature for enhanced functionality." *Micromachines* 15.3 (2024): 391. <https://doi.org/10.3390/mi15030391>
- [26] Wen, Yuanbin, et al. "A Comparative Investigation into the Electronic Structure and Optical Response of NiMoO<sub>4</sub> Modulated by Transition Metal Doping." *ACS omega* 10.42 (2025): 49941-49948. <https://doi.org/10.1021/acsomega.5c06127>
- [27] Wang, Jian, et al. "Synthesis of NiCo<sub>2</sub>S<sub>4</sub>@ NiMoO<sub>4</sub> nanosheets with excellent electrochemical performance for supercapacitor." *Crystals* 12.6 (2022): 821. <https://doi.org/10.3390/cryst12060821>
- [28] Alharbi, S. R., and K. A. Aly. "Electrical and thermoelectric properties of ternary Cu-Ge-Te films." *Journal of Alloys and Compounds* 797 (2019): 710-716. <https://doi.org/10.1016/j.jallcom.2019.05.112>

- [29] Tang, Xiaohui, et al. "Venus flytrap-like hierarchical NiCoMn–O@ NiMoO<sub>4</sub>@ C nanosheet arrays as free-standing core-shell electrode material for hybrid supercapacitor with high electrochemical performance." *Journal of Power Sources* 477 (2020): 228977. <https://doi.org/10.1016/j.jpowsour.2020.228977>