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Photoelectric Synergistic Supercapacitor Constructed by Cerium and Cobalt Co-Doped Zinc Ferrite Cathode and Hydrophilic Carbon Nanotubes

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ABSTRACT

In order to solve the problem of low energy density of existing supercapacitors, this study uses ZnFe_2O_4 as the matrix, through Ce single doping, Co single doping and Ce,Co Double doping modification, combining microwave-assisted reaction and roasting process to prepare flower-like doped ZnFe_2O_4 cathode material, while using arc discharge method and acidification modification to prepare hydrophilic carbon nanotube (CNTs) anode material, and construct an asymmetric supercapacitor and explore its photoelectric properties. The results show that 12 h is the optimal reaction time and 0.5% is the optimal doping ratio. At this condition, the Ce,Co co-doped ZnFe_2O_4 delivers a specific surface area of $126.4\text{ m}^2/\text{g}$, a high specific capacity of 517 F/g at 1 A/g , and a capacity retention of 91.0% after long-term cycling. The assembled Ce,Co- ZnFe_2O_4 /CNTs asymmetric supercapacitor exhibits a capacity retention of 85% after 10,000 cycles, with an energy density of 12.5 Wh/kg and a power density of 536 W/kg . In the photoelectric synergistic charging mode, the specific capacity is increased by 7.2% compared with pure electric charging mode, the specific capacity is increased by 7.2% compared with electric charging alone, and the cycle stability is better, providing key support for the research and development of high-energy supercapacitors. Different from conventional doping strategies reported for ZnFe_2O_4 , this work highlights the synergistic effect of Ce,Co co-doping and photoelectric assistance, which effectively elevates the energy density and cycling stability of the assembled asymmetric supercapacitors.

1. Introduction

The continuous expansion of the worldwide economy and rising population have led to a significant increase in the use of fossil fuels. Such circumstances lead to critical energy shortages and initiate a range of environmental problems, encompassing climate change and pollution. As a result, it's critically important to create renewable energy solutions that are both eco-friendly and sustainable.[1,2] Supercapacitors play a vital role in sectors such as electronics, aerospace, and energy vehicles due to their efficient charging and discharging functions, broad temperature range, and enhanced safety and stability. However, the limited energy density of existing products poses challenges in fulfilling the increasing practical demands of people. As a result, the development of innovative electrode substances for asymmetric supercapacitors is in sync with technological progress and possesses considerable promise for practical application.[3-5] Supercapacitors are classified into two types: pseudocapacitive and electric double layer, each characterized by its distinct charge storage system. The pseudocapacitive variety can retain charge by performing redox reactions on the surfaces of active substances. Such a feature results in an increase in energy density and capacitance, and its irregular configuration further improves its efficiency in energy storage.[6,7] A material's microstructure is a close reflection of its chemical characteristics and its ability to catalyze. Structures at the nanoscale, such as nanosheets, nanorods, nanoneedles, and nanotubes, considerably expand the material's specific surface area due to their distinct geometric properties. This approach results in the creation of diverse ion transit pathways and interaction areas, enhancing its permeability, and concurrently establishes several active sites on the surface, facilitating an extensive interaction between the material and ions. Additionally, this

approach reduces the duration of ion diffusion and improves the material's electrochemical efficiency and usability. Evidently, the substances employed in electrodes are vital in advancing supercapacitor technology.[8-12]

Previous studies have shown that Li and associates. Converted the transition metal Gd into zinc ferrite (ZnFe_2O_4) using a carbon-based composite structure, employing it as a material for electrodes in bendable hybrid supercapacitors. In particular testing scenarios, the doped substance exhibited a substantial specific capacity of 887 F/g, and even after 7000 cycles with a 15 A/g current density, its capacitance retention rate remained at 94.5%, showcasing remarkable cycle stability.[13] The cobalt-doped zinc-based ferrite supercapacitor material studied by Chen et al. has a specific surface area increased from 35 m^2/g of the pure phase to 148 m^2/g . It mainly destroys the spinel crystal structure through doping to increase the specific surface area. In addition to destroying the original lattice structure of ZnFe_2O_4 , the doping strategy of this study also actively introduces oxygen vacancies through double doping of Ce and Co to further expand the specific surface area and enhance electrochemical activity.[14] This study utilizes ZnFe_2O_4 in a matrix, enriched with rare earth elements of Ce and Co, to precisely boost electrochemical efficiency, resulting in a Ce, Co- ZnFe_2O_4 compound with an unstructured porous structure. This design has the ability to generate a variety of redox active sites, thereby improving electron conduction efficiency and laying the foundation for sophisticated energy storage. Owing to their exceptional physical and chemical traits, rare earth elements play a vital role across multiple industries, providing vital support for electronic gadgets, enhancing the core properties of magnetic materials, accelerating catalytic activities, and assisting in the improvement and fine-tuning of optical precision equipment. Given the challenges of low conductivity, limited specific surface area, and augmented

volume in the cycling of ZnFe_2O_4 materials, modifying them using rare earth elements becomes a feasible approach. this approach excels in handling a variety of physical and chemical properties of materials, including crystal creation, surface configuration, specific surface area, electronic conduction efficiency, chemical stability, and general structural stability, to name a few.[15-18] Ce (a rare earth element) and Co (a transition metal), have garnered significant acclaim in electrochemical material innovation due to their unique electronic configurations and improved chemical properties.[19-21] ZnFe_2O_4 , identified as a transition metal oxide with a spinel structure, demonstrates considerable theoretical specificity and the ability to adapt to various environmental scenarios. Zn and Fe, as elemental elements, have the ability to transfer several electrons through alterations in their multivalent states, thereby contributing to the increase in energy density. [22-24]

According to our understanding, cerium (Ce), an element of rare earth elements, has demonstrated distinct advantages in innovating electrochemical materials, credited to its distinctive electronic structure and enhanced chemical characteristics. Simultaneously, the impact of doping with rare earth ions on the effectiveness of metal oxide-based composites is significant, due to their close alignment with intermetallic materials. Not only is ZnFe_2O_4 abundant in resources and environmentally friendly, but it also exhibits strong structural soundness, laying a solid foundation for subsequent doping modification initiatives[25-27]. As a result, the study incorporated Ce and Co elements into the ZnFe_2O_4 matrix, modifying its crystalline structure, electronic state, and active sites on the surface. This method surpassed the limitations of the pure phase ZnFe_2O_4 in terms of energy storage, such as reduced conductivity, insufficient active sites, and limited cycle stability, resulting in simultaneous optimization of the supercapacitor's specific capacity and

cycle length.[28-30]

We selected carbon nanotubes for their excellent hydrophilicity, making them ideal for anode materials. This substance has demonstrated multiple key advantages in electrochemical applications: its hydrophilic groups on the surface significantly enhance the compatibility between electrodes and electrolytes, reduce resistance at the interface, thereby increasing the efficiency of electrolyte ions' movement[31]; the unique structure of the hollow tube allows for several active sites and seamless handling of electrolyte ion insertion and release. Furthermore, it assists in slowing down the change in volume throughout the charging and discharging stages, thereby boosting the electrode's structural steadiness within the designated spectrum[32-34]; Owing to its enhanced electron transfer and uniform chemical properties, this technique improves the electrode's charge transfer efficiency, ensuring the electrode's safety and quick discharge over prolonged durations, thereby meeting the criteria for high-capacity and long-lasting energy storage systems[35]. To sum up, the study successfully synthesized a ZnFe_2O_4 matrix substance with a high purity through careful handling of the preparation process. Following this, the focus transitioned to employing a double-doping approach for collaborative alteration, resulting in the development of a multifaceted variable system. Utilizing the length of doping as a fluctuating element, the effect of Ce, Co double-doping on the elemental ratio was separately examined, addressing the challenges of low energy density and restricted specific surface area linked to doping with single rare earth elements[36,37].

In-depth analysis is conducted on the joint efforts of various components in the dual doping systems, encompassing elements such as managing electronic structures and reconstructing defect sites.

Utilizing X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM),

and electrochemical performance evaluations, this work comprehensively examines how double doping affects the structure, surface electronic state, and reaction dynamics of the ZnFe_2O_4 crystal at the interface. characteristics and robust composition. Despite great progress achieved in doped ZnFe_2O_4 and its composites, most studies only focus on single doping or simple hybridization with carbon materials, and few works realize simultaneous regulation of elemental composition, electronic structure, and photoelectric synergistic

effect.

In this work, Ce,Co co-doped $\text{ZnFe}_2\text{O}_4/\text{CNT}$ composites are designed and synthesized, which can effectively adjust the band structure, introduce abundant oxygen vacancies, and enhance electrical conductivity.

Combined with photoelectric synergy, the energy density and rate performance of the supercapacitor are significantly improved, providing a new strategy for developing high-performance ZnFe_2O_4 -based electrode materials for advanced supercapacitors.

2. Experimental section

2.1 Preparation of ZnFe_2O_4 materials

Reagents: Iron nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), sodium hydroxide (NaOH), nitric acid (HNO_3), cerium nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), ammonia solution ($\text{NH}_3 \cdot \text{H}_2\text{O}$, 25 wt%), absolute ethanol, ethylene glycol, hexamethylenetetramine (HMT), ethylenediaminetetraacetic acid (EDTA), carbon nanotubes (CNTs), and deionized water. All reagents were of analytical grade (AR) and used as received without further purification.

Instruments: 721 UV-visible spectrophotometer, 85-2 digital constant temperature magnetic stirrer; Hitachi S-3400N scanning electron microscope (acceleration voltage 20k V, magnification 20000 times), FEI-Tecnaï-G20 transmission electron microscope; D/max-r BX-ray diffractometer (radiation source Cu $K\alpha$ ray, $\lambda=0.15418\text{nm}$), Working voltage 40 kV, working current 40 mA, scanning range 2θ is $10^\circ\sim 80^\circ$, scanning step 0.02° , scanning speed $6^\circ\cdot\text{min}^{-1}$, solid detector; MULTILAB2000 X-ray photoelectron spectrometer (excitation source Al $K\alpha$ ray, $\lambda=0.8339\text{nm}$), ray energy 1487 eV, line width 1.0 eV, The vacuum degree is $5.0\times 10^{-8}\text{Pa}$, and the binding energy value is corrected with contaminated carbon (C1s, $E_b=284.6\text{eV}$); a PerkinElmer Lambda 35 UV-visible absorption spectrometer (using an integrating sphere, with BaSO_4 as the background, and a scanning speed of $200\text{nm}/\text{min}$) is used to detect the UV-visible diffuse reflectance spectrum of the catalyst[38].

2.2 Preparation of flower-like ZnFe_2O_4

The whole preparation process is divided into three stages as illustrated in Fig. 1 [39-41]. In Stage I (Sol-Gel Formation), 2.5 g $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 1.23 g $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved in 40 mL deionized (DI) water under magnetic stirring at 300 rpm for 30 min to prepare a homogeneous mixed metal salt solution; 25 wt% ammonia solution was then added dropwise under stirring to adjust the system pH to 3–4, followed by the addition of 10 mL ethylene glycol, and the resulting mixture was continuously stirred in a 60°C water bath for 2 h to form a transparent sol. The obtained sol was sealed and thermally aged at 80°C for 12 h to complete the sol-to-gel transition and obtain a bulk wet gel. In Stage II (Hydrothermal Synthesis), the aged gel block was broken up and fully redispersed in 30 mL DI water under magnetic stirring, after which hexamethylenetetramine (HMT, acting as a morphology-directing agent) was incorporated and the suspension was magnetically stirred for another 30 min to achieve uniform dispersion; the well-mixed suspension was transferred into a polytetrafluoroethylene (PTFE)-lined stainless steel autoclave and subjected to hydrothermal treatment at 180°C for 12 h, and the autoclave was subsequently cooled naturally to room temperature after the reaction finished. In Stage III (Post-Treatment & Calcination), the solid precipitate generated from hydrothermal reaction was separated by centrifugation, and the sediment was alternately washed with DI water and anhydrous ethanol for three cycles to remove residual inorganic ions and organic impurities; the cleaned precipitate was dried in an oven at 60°C

for 12 h to yield flaky precursor powder. Finally, the dried precursor powder was calcined in a muffle furnace at 800 °C for 2 h, and flower-like

ZnFe_2O_4 microstructured material was collected after natural furnace cooling to ambient temperature.

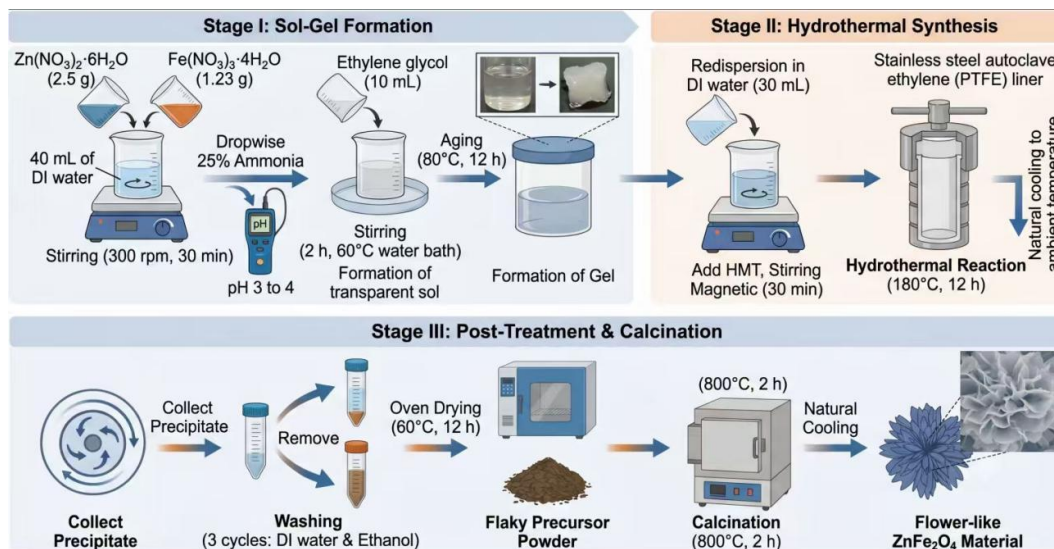


Fig. 1 Schematic diagram of the preparation process of flower-shaped ZnFe_2O_4 electrode material

2.3 Preparation of flower-like Ce-doped ZnFe_2O_4 , flower-like Co-doped ZnFe_2O_4 , flower-like Ce and Co double-doped ZnFe_2O_4

The fabrication procedure of Ce- ZnFe_2O_4 is illustrated in Fig. 2. Firstly, an appropriate amount of pre-synthesized ZnFe_2O_4 solid powder was added into a beaker filled with deionized water, and the system was stirred continuously until the powder was fully dispersed to form a uniform aqueous suspension of ZnFe_2O_4 . Then analytical-grade EDTA solution, acting as the metal ion complexing agent, was slowly dropped into the suspension under sustained stirring at a standard ZnFe_2O_4 -to-EDTA molar ratio of 1:1; stirring was maintained until the added EDTA was fully dissolved. Afterwards, a stoichiometric amount of cerium precursor ($\text{Ce}(\text{NO}_3)_3$ or CeCl_3) was incorporated into the above mixture, which was stirred thoroughly with a glass rod for 20–30 min to achieve a homogeneous mixed solution. The well-blended liquid was then transferred into a microwave reaction vessel, which was covered and sealed to carry out microwave-assisted reaction under controlled conditions: microwave output power of 500–800 W, reaction temperature of 80–100 °C, and holding time of 30–45 min.

After the microwave treatment finished, the sealed vessel was left to cool naturally down to room temperature (25 °C). The cooled mixture was transferred into centrifuge tubes and separated by centrifugation at 8000 r/min for 10 min to harvest the solid sediment at the bottom of the tubes. The collected solid was subjected to three repeated washing cycles using a 1:1 volume ratio mixture of deionized water and absolute ethanol, with stirring and centrifugation implemented in each cycle to wash away surface residual impurities and unreacted starting reagents. After purification, the washed solid was placed in a muffle furnace and calcined at a constant temperature of 500 °C for 40 min under air atmosphere. The furnace was then naturally cooled until its internal temperature dropped below 100 °C, after which the target Ce- ZnFe_2O_4 powder product was retrieved. Additionally, Co single-doped Co- ZnFe_2O_4 and Ce/Co co-doped Ce,Co- ZnFe_2O_4 composite materials can be fabricated following this identical microwave-assisted preparation protocol.

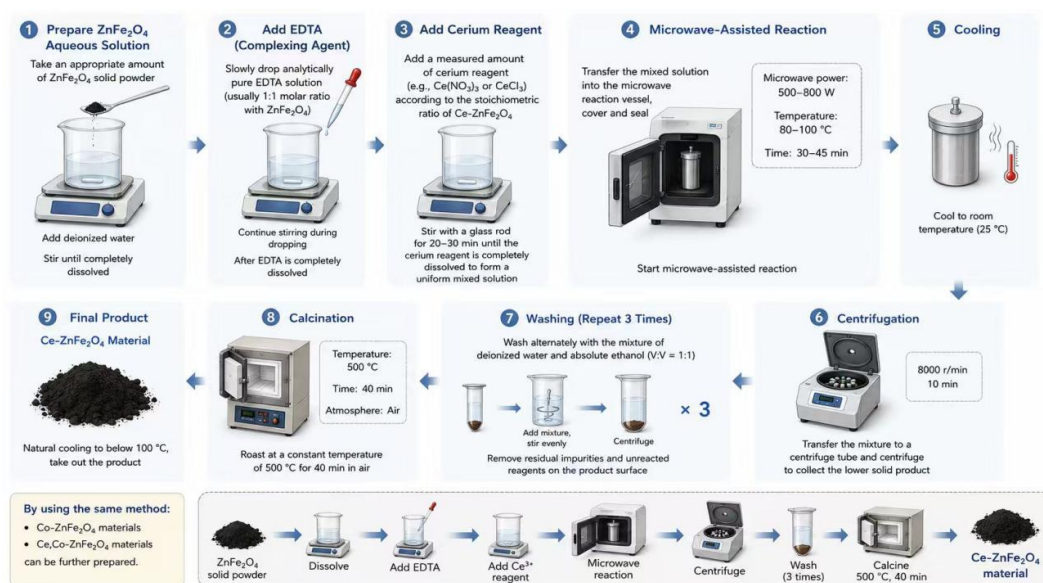


Fig. 2 Preparation of flower-like Ce-doped ZnFe_2O_4 , flower-like Co-doped ZnFe_2O_4 , flower-like Ce and Co double-doped ZnFe_2O_4

2.4 Preparation of hydrophilic carbon nanotubes

As illustrated in Fig. 3, the preparation of carbon nanotubes (CNTs) consists of three continuous procedures: arc-discharge synthesis, aqueous dispersion with ultrasonic exfoliation, and vacuum drying followed by tube furnace thermal post-treatment. In the arc-discharge synthesis process (Section A), the reactor chamber was evacuated and filled with high-purity argon (Ar, purity $\geq 99.999\%$) to construct an oxygen-free inert atmosphere; graphite rods were used as the anode and cathode, and arc plasma generated between electrodes induced carbon vapor deposition on the cathode to form high-crystallinity CNTs with ordered lattice structures. For the dispersion and ultrasonic exfoliation step (Section B), 250 mg as-prepared CNT powder was accurately weighed using an electronic balance with 0.1 mg precision and added into a clean beaker containing 50 mL deionized water. The mixture was magnetically stirred at 300–500 r/min for 60–90 min for preliminary dispersion, and the crude suspension was further treated by a probe-type ultrasonic cell disrupter at 300–500 W for 60 min under room-temperature cooling conditions to break CNT agglomerates and obtain a uniformly dispersed aqueous suspension. In the post-treatment stage (Section C), the well-dispersed CNT suspension was transferred into a petri dish and vacuum-dried at 60–80 °C under a vacuum of -0.08 to -0.09 MPa for 8–12 h to fully

remove water and acquire dry CNT powder. The dried CNT powder was loaded into an alumina boat and placed in a tube furnace, with high-purity Ar ($\geq 99.999\%$) flowing at 80 sccm as protective shielding gas. The furnace was heated from room temperature to 500 °C at a ramp rate of 5 °C/min and held isothermally at 500 °C for 140 min for thermal modification, yielding thermally treated CNT samples.

As a typical one-dimensional carbon nanomaterial, CNTs possess large specific surface area and unique pore structures, making them promising candidates for electrical double-layer capacitors. Nevertheless, the intrinsically hydrophobic surface of pristine CNTs leads to poor electrolyte wettability and reduced specific capacitance in liquid electrolytes, restricting their practical energy-storage applications. The tube furnace thermal treatment under pure Ar at 500 °C merely removes adsorbed moisture and weakly bound surface groups, which cannot introduce hydrophilic functional groups to improve surface wettability. Therefore, supplementary acidification modification is adopted in this work to functionalize CNT surfaces, independent of the thermal treatment route shown in Fig. 3. The acidification process was carried out at 80 °C with mixed acid solution; abundant oxygen-containing functional groups (including hydroxyl, carboxyl and carbonyl groups) were grafted onto CNT

surfaces after acid etching. These polar oxygen groups greatly enhance the hydrophilicity and surface wettability of CNTs, and contribute extra pseudocapacitance apart from electrical double-layer capacitance at the electrode-electrolyte interface. After acid etching, the CNT precipitates were repeatedly washed with deionized water until neutral pH, then dried in a blast drying oven at 80 °C for 8 h. After natural cooling to room temperature, hydrophilic functionalized CNTs with excellent water dispersibility were finally

obtained. The two SEM images inserted in Fig. 3 display the micro-morphology of pristine arc-discharged CNTs and acid-modified CNTs, respectively. Comparative observation reveals that acid etching roughens CNT surfaces and destroys the original smooth tube walls, while the one-dimensional tube aspect ratio remains nearly unchanged; this surface morphological variation originates from the grafting of oxygen-containing functional groups and mild acid corrosion on CNT outer walls [42–45].

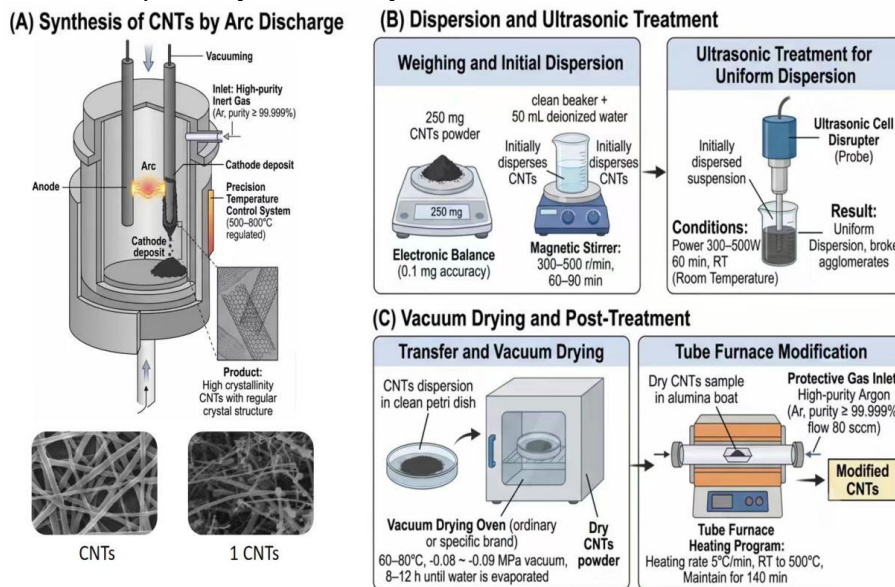


Fig. 3 Preparation diagram of hydrophilic carbon nanotubes

2.5 Hydrophilicity test of hydrophilic carbon nanotubes

According to Wenzel's theory, the ability of substances to attract water is influenced by both their surface texture and the angle at which they come into contact with water. Without external pressure, the presence of surface tension transforms a droplet into a spherical shape; on the flip side, the final shape of this droplet is formed by the interplay of liquid molecules and the connection between solid and liquid. The contact angle is defined as the angle created by the droplet's unbound dispersion and its firm surface. In the Wenzel model, the formula for water contact angle is expressed as $\cos\theta_w = r\cos\theta$, with

r representing the surface roughness ratio (the proportion of the real solid to the projected solid surface area), and θ denoting the rough surface contact angle. Precisely, if θ is less than 90° , the material's surface texture becomes more uneven, θ_w diminishes, and lyophilicity intensifies; conversely, when θ exceeds 90° , this roughness augments θ_w , thereby amplifying lyophobicity. Coupled with the outcomes shown in the Fig. In Fig. 4(a)–(e), the angle at which the 1CNTS material contacts water post-acidification treatment measures 6° . The information verifies the material's hydrophilic nature⁴⁶.

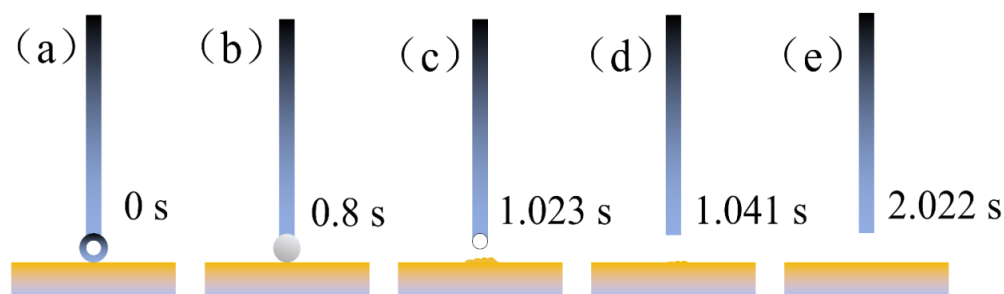


Fig. 4 Hydrophilicity test of hydrophilic carbon nanotubes

2.6. Formulas used in this work

The formulas required in the experiment are as follows:

$$C_s = it/mV$$

$$(1) \quad P = 3600E/\Delta t$$

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

(3) C_s (F/g) represents the specific capacitance, Δt (s) represents the discharge time, i (A) represents the

current density, ΔV (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.

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

$$i = avb \quad (5)$$

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 $\log(v)$. $I(v)$, v , k_1v and k_2v represent the current effect, scan rate, capacitive process and diffusion control process respectively.

3 Physical characterization and electrochemical performance measurement of Ce-ZnFe₂O₄ nanosheet electrode

During the early phase of the reaction (2 hours Fig. 5 a), the material under observation shows a chaotic particle structure, with the arrangement of these particles being disorganized and uneven, complicating the creation of adequate electrochemically active sites for it. Over time, the material evolves from a stratified form to a spherical one, accompanied by a notable rise in surface texture. As the duration of the reaction extended to 4 hours, as depicted in the Fig. 5 b), despite the gradual formation of the lamellar structure, aggregation was not evident; the brief reaction time at this point resulted in inadequate substance migration and diffusion, leaving the crystal structure incompletely formed. Consequently, this led to a reduced specific surface area, diminished porosity, and an overall material structure that was comparatively lax. This became evident when the reaction duration extended to 8 hours (as depicted in the Fig. 5 c),

there's a gradual shift of the material from the nucleation phase to the crystal growth phase, leading to a more compact arrangement of layers. An expanded specific surface area leads to more effective electron transfer and ion diffusion routes, thus greatly improving the material's electrochemical characteristics. Extending the duration of the reaction to 12 hours, as depicted in the Fig. 5 d), over time, the lamellar formation stabilizes and crystal development attains its ideal form, leading to a consistent and systematic layering of the substance. During this phase, zinc ferrite's specific surface area attains its peak, and its lamellar formation is dense while maintaining suitable pores. This process aids in sufficient electrolyte absorption and guarantees effective ion movement, striking a perfect equilibrium between the material's shape and its electrochemical efficiency. Nonetheless, as the duration of the reaction extended to 16 hours (Fig. 5 e) plus 20

hours (Fig. 5 f), as the material progressed to the overgrowth phase, the lamellar formation either overlapped or suffered partial damage, leading to a reduction in the specific surface area; this overaccumulation impeded the electrolyte's penetration and decreased the count of electrochemical active sites exposed. Concurrently, overgrowth leads to grain coarsening, resulting in an overly dense lamellar structure or defects, thus diminishing the material's overall efficacy. To sum up, the

findings from the morphology analysis indicate that a 12-hour period is most suitable for zinc ferrite to achieve the ideal lamellar formation. In this particular timeframe, the crystal's structure demonstrates stability and adequate growth, offering a substantial specific surface area and suitable porosity, thereby creating an advantageous setting for electrolyte infiltration and charge movement, thereby enhancing the material's electrochemical characteristics.

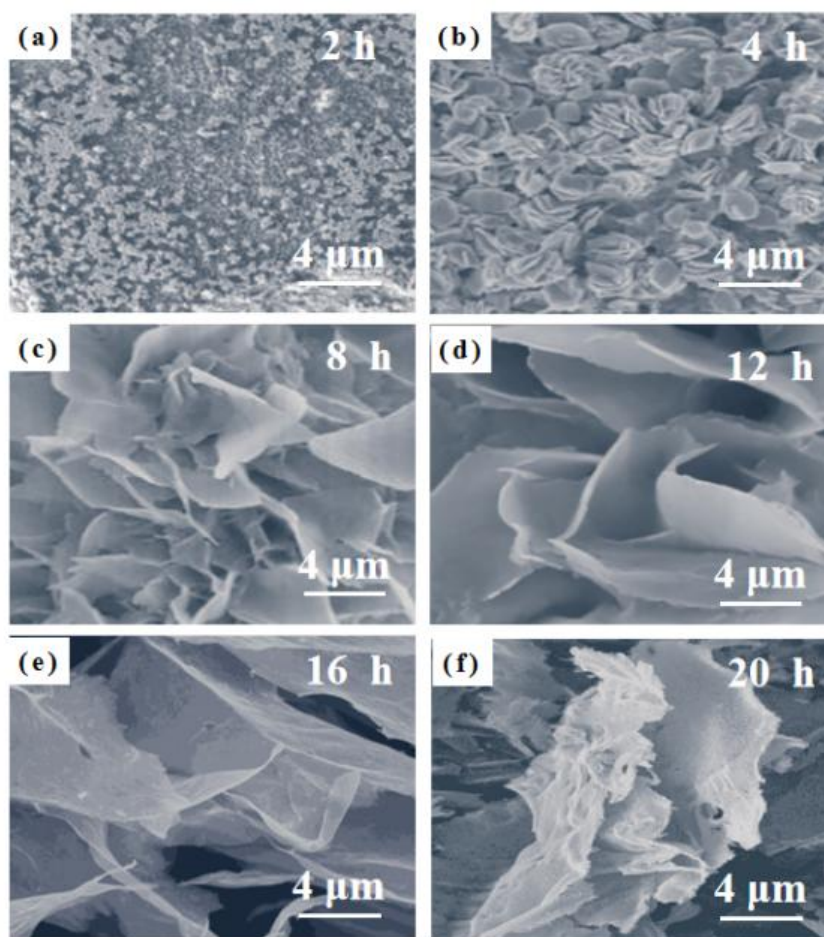


Fig. 5 Scanning electron microscope (SEM) images of ZnFe_2O_4 under different reaction times, (a) 2 h; (b) 4 h; (c) 8 h; (d) 12 h; (e) 16 h; (f) 20 h

The nitrogen adsorption-desorption testing technique was employed to thoroughly examine the specific surface area (BET) and the distribution of pore sizes in Ce- ZnFe_2O_4 doped and pure ZnFe_2O_4 materials. Fig 6 displays the outcomes of the tests, whereas Fig 6 (a) through (d) illustrate the adsorption-desorption isotherms

and the distribution curves of pore sizes for these four substances, in that order. Based on the configuration of the isotherms, these four substances exhibit common traits of type IV isotherms, including increased saturation adsorption pressure, a mild extension platform, and a notable rise in curve slope at high relative pressure; the classification of the hysteresis loops

in both isotherms as H3 type further validates the mesoporous nature of Ce-ZnFe₂O₄ and ZnFe₂O₄. Notably, the clear hysteresis loop in unadulterated ZnFe₂O₄ emerges solely within the 1.0-1.2 relative pressure spectrum, in contrast to the 0.5% Ce-ZnFe₂O₄ hysteresis loop, which is present at approximately 0.6 relative pressure. The variance indicates that doping with Ce elements can efficiently facilitate the initial creation of pores in the nanosheet structure of the material, thereby augmenting the pore count. The BET theoretical analysis indicates that the combined impact of the reduced grain size and mesoporous composition of the four substances, ZnFe₂O₄, 0.1% Ce-ZnFe₂O₄, 0.5% Ce-ZnFe₂O₄, and 0.8%, led to specific surface areas of ZnFe₂O₄ measuring 68.4m²/g, 92.3m²/g, 112.7m²/g, and 98.5m²/g, respectively. The information verifies that doping with Ce beneficially impacts the expansion of ZnFe₂O₄'s specific surface area - an expanded specific surface area not only creates more reactive areas for electrochemical processes but

also accelerates the transfer of electrolyte ions in the substance. The pore size distribution curve reveals that the primary diameters of ZnFe₂O₄, 0.1% Ce-ZnFe₂O₄, 0.5% Ce-ZnFe₂O₄, and 0.8% Ce-ZnFe₂O₄ are roughly 26nm, 28nm, 32nm, and 29nm, aligning with the previously mentioned mesoporous structure analysis; furthermore, 0.5% The distinct peak in Ce-ZnFe₂O₄'s pore size distribution curve at approximately 7nm suggests a notable rise in small pores near 7nm, which can restrict grain growth to some degree, thus enlarging the material's specific surface area. To summarize, doping Ce enhances both the specific surface area and the count of tiny pores, creating numerous active areas for electrochemical reactions. It also speeds up the dissolution of electrode materials in the electrolyte, reduces the transmission routes of electrons and ions, and markedly boosts their efficiency, thereby establishing a robust structural base for refining the material's electrochemical characteristics[46,47].

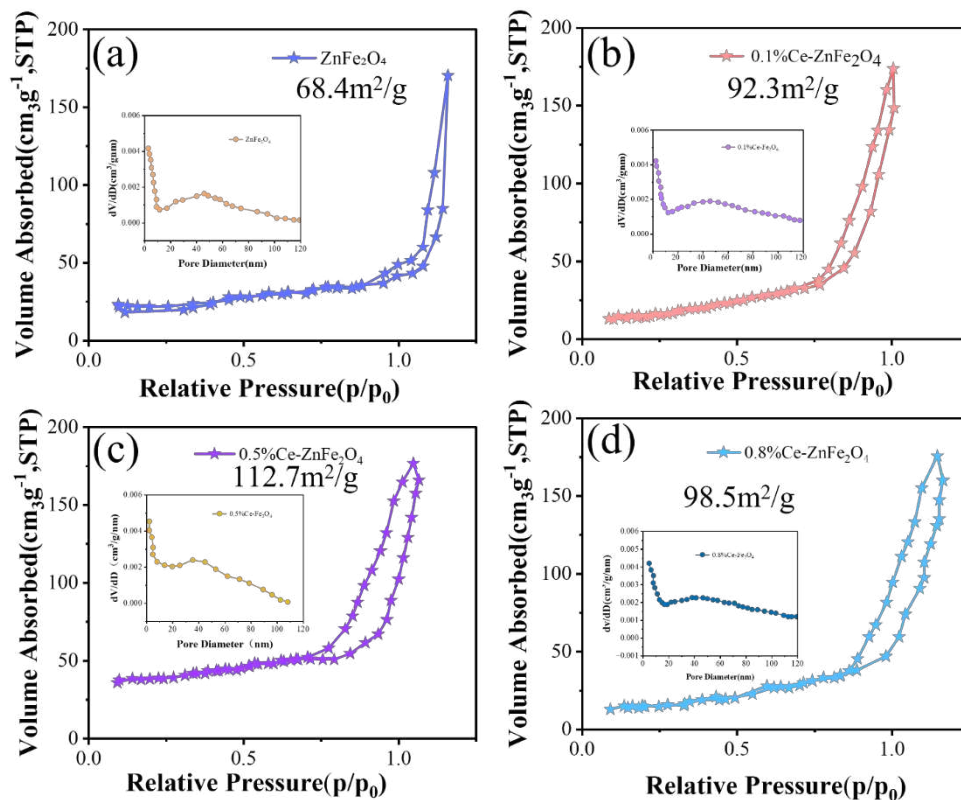


Fig. 6 N₂ adsorption-desorption isotherms and pore size distribution of ZnFe₂O₄, 0.1% Ce-ZnFe₂O₄, 0.5% Ce-ZnFe₂O₄ and 0.8% Ce-ZnFe₂O₄

The examination of the electrochemical properties of the electrode substances took place in a tri-electrode setup, employing 6M KOH as the electrolytic substance. A platinum sheet was used for the counter electrode, Hg/HgO as the

benchmark electrode, and the ready-made material acted as the active electrode. Fig. 7 depicts the associated schematic of a tri-electrode setup.

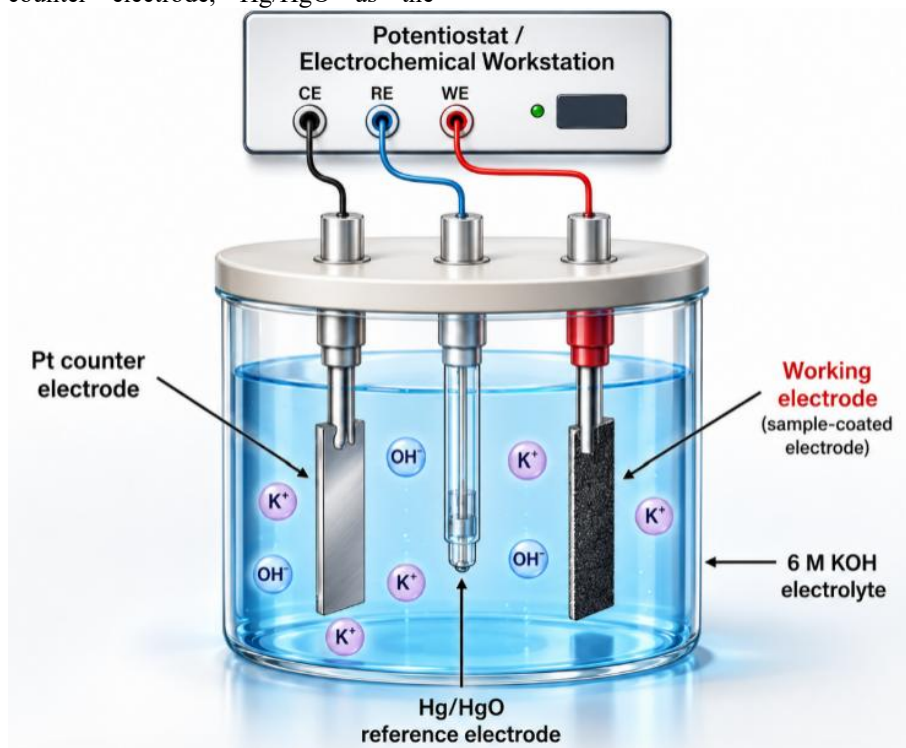


Fig. 7 Three-electrode system diagram

Following the performance evaluation of the undoped $ZnFe_2O_4$ substance, systematic assessments of its electrochemical efficiency were conducted to elucidate Ce doping's regulatory impact on the material's electrochemical properties. Fig. 8 (a) The cyclic voltammetry (CV) graph reveals that the CV graphs for Ce-infused $ZnFe_2O_4$, prepared at intervals of 4 hours, 8 hours, 12 hours, and 16 hours, display nearly rectangular capacitive properties. Over the course of the preparation period, there were consistent alterations in the curve's area, culminating in its peak value at 12 hours. Introducing Ce results in the creation of numerous active sites and flaws, coupled with the material's porous nature, significantly speeding up the movement of electrons and ions in the electrolyte, enabling the material's electrochemical properties to achieve their peak within a 12-hour period. The graph depicting charge-discharge in the Fig. 8 (b) demonstrates that, given identical current density

scenarios, the release duration of Ce-doped $ZnFe_2O_4$, synthesized after 12 hours, is markedly extended compared to other sample durations. The prolonged discharge clearly showcases its superior charge and discharge properties, a direct result of Ce doping that enhances the electronic conduction network and boosts the efficiency of charge storage and release. Fig. 8 (c) represents a histogram illustrating specific capacity. Post-calculation, the distinct capacities of the samples at 4, 8, 12, and 16 hours stand at 291 F/g, 342 F/g, 439 F/g, and 378 F/g, in that order. At 12 hours, the specific capacity peaks, underscoring the notable enhancement in energy storage due to Ce doping - this doping augments the count of active sites while concurrently altering the crystal structure to improve ion insertion/extraction reversibility, thereby substantially boosting the specific capacity. Fig. 8 (d) displays the electrochemical impedance spectrum (EIS). After 12 hours of preparation, the sample exhibits the

least impedance in the high-frequency area, and the Nyquist plot's linear gradient peaks in the low-frequency zone, signifying minimal charge transfer resistance and rapid ion diffusion. The reason behind this is that Ce doping modifies the electronic configuration of ZnFe_2O_4 , reduces the energy barrier for charge transmission at the interface, and facilitates a more fluid movement

of ions and electrons. Consequently, doping with Ce markedly enhances ZnFe_2O_4 's electrochemical efficiency through the addition of active sites, improved electron conduction, preservation of the porous structure, among other processes, achieving peak performance after a 12-hour preparation period.

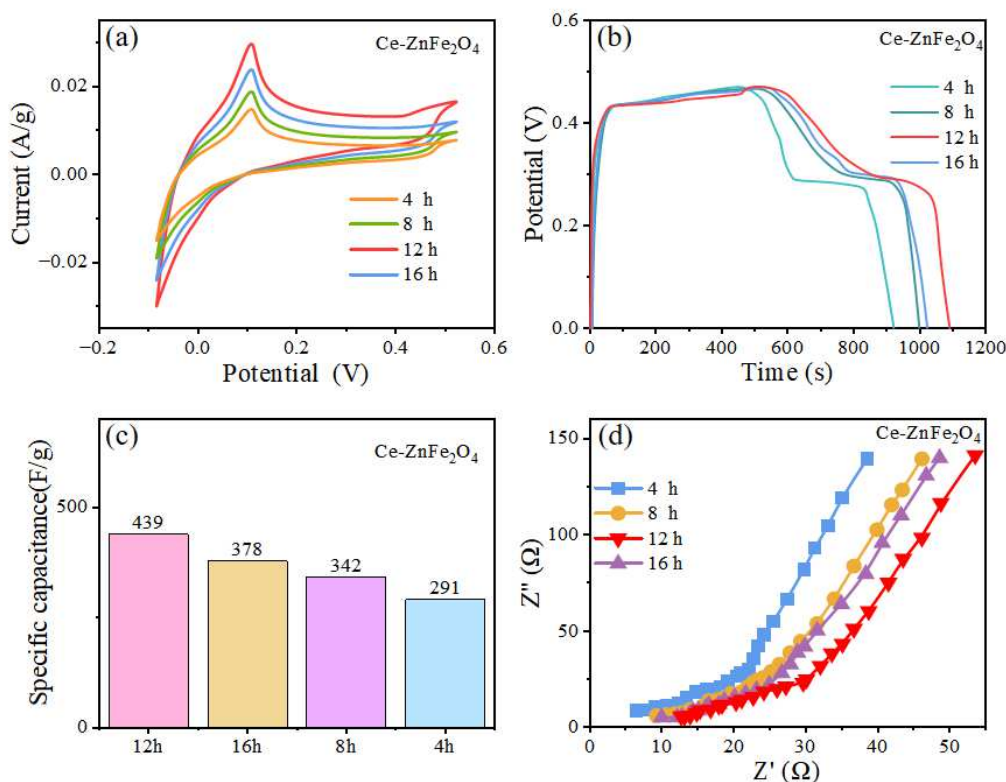


Fig. 8 (a) Cyclic voltammetry (CV) curves of $\text{Ce-ZnFe}_2\text{O}_4$ at 4 hours, 8 hours, 12 hours and 16 hours; (b) $\text{Ce-ZnFe}_2\text{O}_4$ at 4 hours, 8 hours Galvanostatic charge and discharge (GCD) curves at 4 hours, 12 hours and 16 hours; (c) $\text{Ce-ZnFe}_2\text{O}_4$ at 4 hours, 8 hours, 12 hours, 16 hours and a current density of 3 Specific capacity diagram at A/g; (d) Impedance diagram of $\text{Ce-ZnFe}_2\text{O}_4$ at 4 hours, 8 hours, 12 hours, and 16 hours.

This research aimed to investigate how the Ce doping ratio influences material electrochemical characteristics by performing electrochemical experiments on four distinct samples: ZnFe_2O_4 , 0.1% $\text{Ce-ZnFe}_2\text{O}_4$, 0.5% $\text{Ce-ZnFe}_2\text{O}_4$, and 0.8% $\text{Ce-ZnFe}_2\text{O}_4$. Pertinent information is depicted in the Fig. 9; initially, the conduct of charge storage was examined via cyclic voltammetry (CV) analysis, and the CV depicted in Fig. 9 (a) illustrates that with the rise in Ce doping levels, there's a gradual expansion in the area encompassed by the CV curve of the $\text{Ce-ZnFe}_2\text{O}_4$ specimen, verifying Ce doping's substantial impact on enhancing the material's

electrochemical efficiency, with all $\text{Ce-ZnFe}_2\text{O}_4$ specimens exhibiting clear redox peaks (or bulges) within the -0.3V-0.2V potential spectrum, indicative of their usual pseudocapacitance traits. This finding was further corroborated by the galvanostatic charge and discharge (GCD) test. Fig. depicts the GCD curve at a scanning speed of 4mV/s. Fig. 9 (b) illustrates that 0.5% $\text{Ce-ZnFe}_2\text{O}_4$ exhibits the most extended duration of charge and discharge, along with superior charge and discharge efficiency. By integrating the formula for specific capacitance computation with experimental data, one can deduce that the distinct capacitances of the four specimens at a

3A/g current density amount to ZnFe_2O_4 . 297F/g, 0.1% Ce- ZnFe_2O_4 at 332F/g, 0.5% Ce- ZnFe_2O_4 at 422F/g, 0.8% Ce- ZnFe_2O_4 at 358F/g (Fig. 9 (c)), it's evident that the ideal Ce Doping ratio is 0.5%, with the specific capacitance peaking at this juncture; in terms of structural and performance correlation, Ce- ZnFe_2O_4 's specific surface area markedly exceeds that of solely ZnFe_2O_4 . An expanded specific surface area enhances its ability to absorb additional charges, consequently boosting its electrochemical efficiency and chemical characteristics. The test of electrochemical impedance spectroscopy (EIS), as depicted in the Fig. 9 (d), with a testing frequency span of 5Hz to 100Hz, primarily serves to assess the electrode's efficiency in charge transfer.

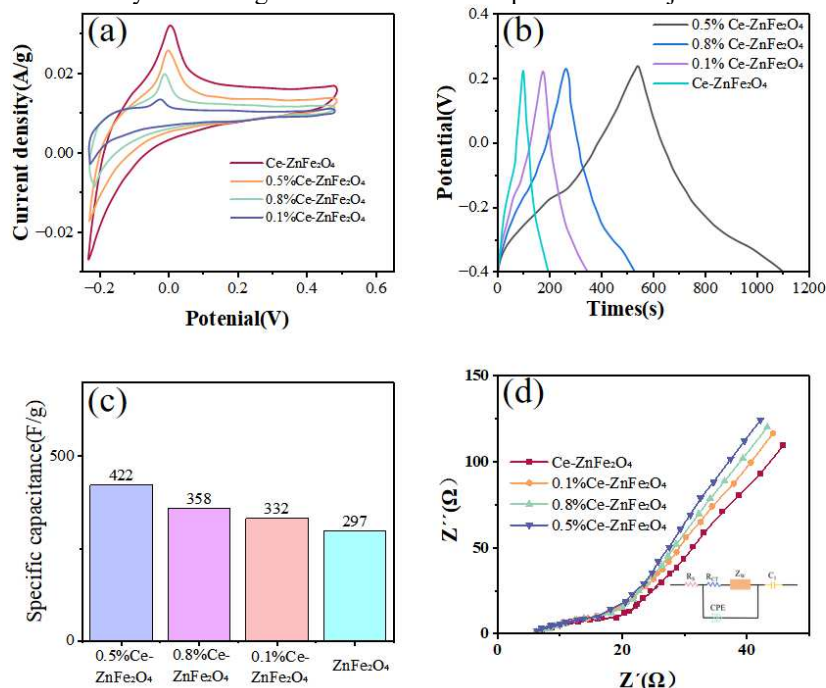


Fig. 9 (a) Cyclic voltammetry (CV) curves of ZnFe_2O_4 , 0.1% Ce- ZnFe_2O_4 , 0.5% Ce- ZnFe_2O_4 and 0.8% Ce- ZnFe_2O_4 ; (b) ZnFe_2O_4 , 0.1% Ce- ZnFe_2O_4 , 0.5% Galvanostatic charge and discharge (GCD) curves of Ce- ZnFe_2O_4 and 0.8% Ce- ZnFe_2O_4 at 4 mV/s; (c) ZnFe_2O_4 , 0.1% Ce- ZnFe_2O_4 , 0.5% Ce- ZnFe_2O_4 and 0.8% Ce- ZnFe_2O_4 at a current density of 3 A/g; (d) Impedance diagram of ZnFe_2O_4 , 0.1% Ce- ZnFe_2O_4 , 0.5% Ce- ZnFe_2O_4 and 0.8% Ce- ZnFe_2O_4 .

The research utilized an electrochemical workstation for performing electrochemical experiments on the Ce- ZnFe_2O_4 electrode within a KOH alkaline electrolyte. The voltage range was established between -0.4V and 0.6V, with the collection of cyclic voltammetry (CV) curves occurring at scanning speeds of 5, 10, 20, 30, 50, and 80 mV/s. The outcomes are depicted in the

Within the low-frequency range, the 12-hour preparation of Ce- ZnFe_2O_4 reveals a vertically aligned line and a steeper incline, indicating a reduced Warburg impedance and enhanced capacitance, aiding in the spread of electrolyte ions and electrons, refining the material's chemical characteristics, and hastening the reaction. In the high-frequency range, the semicircle size of the sample is significantly reduced, highlighting its low resistance to electron transfer and higher conductivity. Simultaneously, the EIS analysis of 0.5% Ce- ZnFe_2O_4 shows its capacitive efficiency more closely matches that of an ideal supercapacitor, prompting the choice of Ce- ZnFe_2O_4 , developed over a 12-hour period, as the experimental subject.

Fig 10 (a). The examination of the test curves reveals that the CV curves for Ce- ZnFe_2O_4 at different scanning velocities display a shape that is largely non-rectangular, with all displaying clear redox peaks. This characteristic aligns with the typical characteristics of pseudocapacitive substances, indicating their ability to store charge in a pseudocapacitive manner. Fascinatingly, as

the scanning velocity escalates from 5 mV/s to 80 mV/s, there's a consistent linear increase in the peak current across all curves, with minimal alteration in their general visual form and an absence of noticeable distortion or peak shift. This occurrence demonstrates that Ce-ZnFe₂O₄ is capable of rapidly engaging in electrochemical processes at varying scanning speeds and exhibits superior reaction rates. This also indicates the material's robust structural integrity and its electrochemical efficiency remains unaffected by variations in the scanning speed.

Fig 10 (a) - (c) displays the distinct outcomes of the capacitance tests at scanning speeds of 5, 10, 20, 30, 50, and 80 mV/s. The respective specific capacitance figures are 239, 268, 291, 338, 376, and 437 F/g. The link between capacitance and scanning velocity is elucidated thus: with an increase in scanning speed, there's a corresponding extension in discharge duration, enhancing the active material's reactivity; furthermore, a rapid scanning speed can make the duration of electrode-electrolyte contact a crucial determinant. Despite its reliance on the speed of scanning, the material maintains outstanding electrochemical characteristics.

In this context, 'i' denotes the maximum current and 'v' the rate of scanning. a remains constant, while b is derivable via the functional correlation between log (i) and log (v). The symbols I (v), v, k₁v, and k₂v symbolize the current effect, scanning speed, capacitance procedure, and diffusion control mechanism, in

that order. The research delved deeper into the diffusion phenomenon and the dynamic properties of Ce-ZnFe₂O₄ nanomaterials. Fig 10 (d) illustrates the linear adjustment chart for log (i) and log (v). Both exhibit a strong linear correlation. As per the evaluative criteria of the equation $i = av^b$: diffusion control prevails at $b=0.5$, while capacitance control takes precedence at $b=1.0$. This research reveals that the b values for the anode and cathode stand at 0.77 and 0.80, respectively, nearing 1. Fig 10 illustrates the rate of pseudocapacitance contribution across various scanning speeds. Fig 10 (e), indicating that the primary regulation of the Ce-ZnFe₂O₄ nanomaterial is through surface pseudocapacitance, complemented by diffusion control. Both modes of control operate in a synergistic manner. Fig 10 (f) illustrates the present state of managing surface and diffusion at a rate of 10 mV/s. The roles of pseudocapacitance and diffusion control capacitance are analyzable via the empirical equation $i = k_1v + k_2v^{1/2}$, where k_1v denotes pseudoapacitance control and $k_2v^{1/2}$ indicates diffusion control. With the escalation of the scan rate, there's a steady rise in the rate at which capacitance control is contributed; conversely, at reduced scanning speeds, the material's capacitance traits are predominantly influenced by the diffusion process. As the scanning speed escalates to 140 mV/s, pseudocapacitance control's contribution rate can climb to 75%, verifying the dynamic properties of the Ce-ZnFe₂O₄ material.

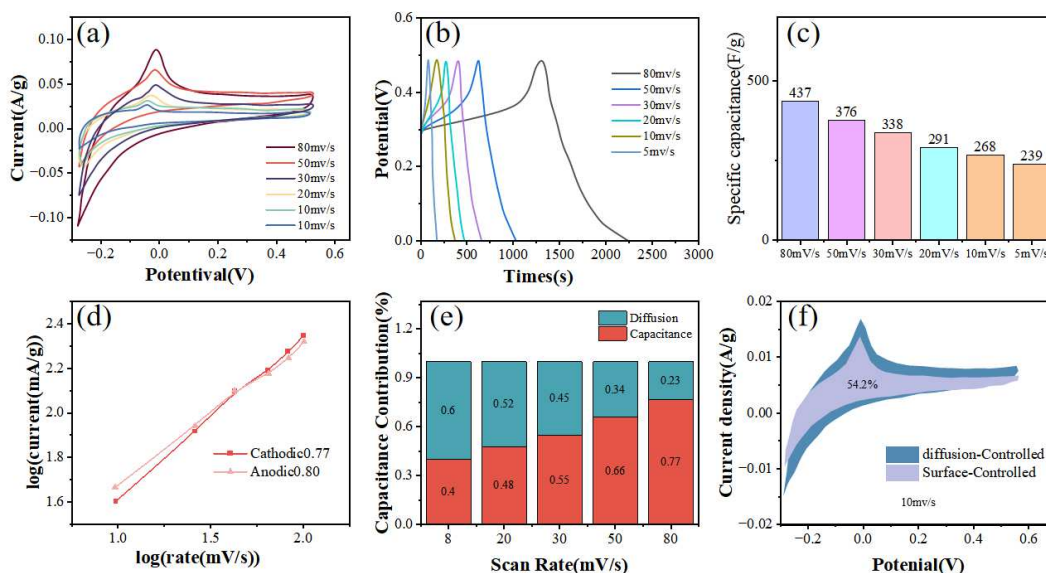


Fig. 10 (a) - (c) displays the distinct outcomes of the capacitance tests at scanning speeds of 5, 10, 20, 30, 50, and 80 mV/s. The respective specific capacitance figures are 239, 268, 291, 338, 376, and 437 F/g. The link between capacitance and scanning velocity is elucidated thus: with an increase in scanning speed, there's a corresponding extension in discharge duration, enhancing the active material's reactivity; furthermore, a rapid scanning speed can make the duration of electrode-electrolyte contact a crucial determinant. Despite its reliance on the speed of scanning, the material maintains outstanding electrochemical characteristics.

4 Physical characterization and electrochemical performance measurement of Co-ZnFe₂O₄ nanosheet electrode

Fig. 10 (a) alongside the Figure. Fig. 10 (b) displays scanning electron microscopy (SEM) visuals of Ce-doped ZnFe₂O₄ and Co-doped ZnFe₂O₄ single-doped electrode substances, in that order. The image distinctly shows that each of the two materials possesses well-defined boundaries. Both display structures of sheets at the nanoscale. Each sheet maintains a fairly uniform size, with a mildly wavy surface, and a few sheets are arranged in a loosely layered manner. The interweaving of these sheet-like formations results in a floral porous look, yet the compactness of this structure could adversely impact electron movement. The details of element distribution are presented in the Figure. The data in Fig. 10 (e) to (f) reveal that the ZnFe₂O₄ material, doped with Ce, comprises four distinct

elements: Zn, Ce, O, and Fe. These elements are uniformly dispersed within the ZnFe₂O₄ nanostructure, aligning with the material's general structural configuration, without any clear zones of element concentration or reduction. The depiction is presented in the figure. Fig. 10 (g)~(j) illustrates the composition of four elements in the Co-doped ZnFe₂O₄ substance: Zn, Co, O, and Fe. In the ZnFe₂O₄ nanostructure, every component is evenly dispersed, aligning with the material's general structural contour, without notable enrichment or reduction of elements. The results of the aforementioned analysis indicate the absence of additional impurities in the two single-doped substances with ZnFe₂O₄ we created, demonstrating their high purity.

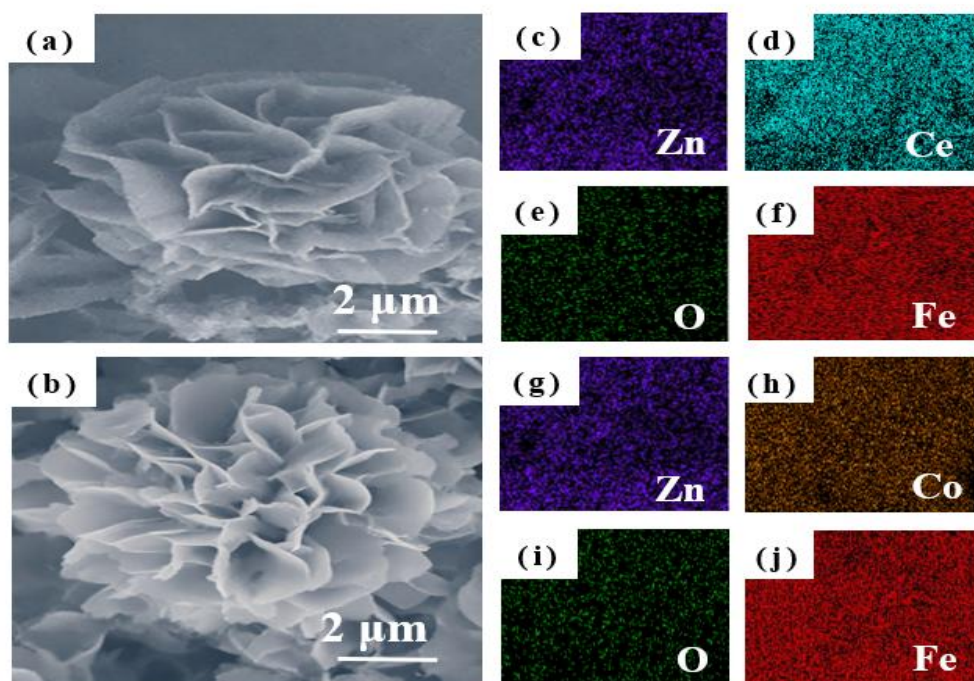


Fig. 11 Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) elemental distribution maps of different samples. (a) Flower-like Ce doped ZnFe_2O_4 ; (b) Flower-like Co doped ZnFe_2O_4 ; (c)-(f) The distribution diagrams of Zn, Ce, O and Fe elements of flower-like Ce doped ZnFe_2O_4 respectively; (g)-(j) The distribution diagrams of Zn, Co, O and Fe elements of flower-like Co-doped ZnFe_2O_4 respectively.

Through nitrogen adsorption and desorption experiments, we conducted a detailed analysis of the specific surface area (BET) and the range of pore dimensions in unadulterated ZnFe_2O_4 and Co- ZnFe_2O_4 doped materials, as illustrated in the Fig. 12 Thirteen segments from (a) through (d). The quartet of compounds demonstrates typical type IV adsorption-desorption isotherms, characterized by high saturation adsorption pressure, a gentle extension platform, and a significant increase in the high relative pressure spectrum's gradient, where all hysteresis loops are H3 type, underscoring their mesoporous characteristics; especially, the hysteresis loop of ZnFe_2O_4 appears in the range of 1.0-1.2, and the presence of 0.5% Co- ZnFe_2O_4 near 0.6 suggests the influence of Co doping in accelerating pore formation in nanosheets and their volume. BET analyses reveal that ZnFe_2O_4 , 0.1% Co- ZnFe_2O_4 , 0.5% Co- ZnFe_2O_4 , and 0.8% Co- ZnFe_2O_4 each possess distinct surface areas of 68.4m²/g,

90.1m²/g, 110.3m²/g, and 97.5m²/g, in that order. Studies have verified that doping with Co markedly enlarges the specific surface area, leading to a rise in electrochemical reaction active sites and accelerating electrolyte ion transmission; the distribution curve of pore sizes for these four substances is around 25nm, 27nm, 31nm, and 29nm, aligning with the mesoporous structure's findings, and a distinct peak at 8nm in 0.5% Co- ZnFe_2O_4 suggests that more small holes can curb crystal grain growth and expand its specific surface area. To sum up, Co doping generates numerous active sites for electrochemical processes by enlarging the specific surface area and increasing the count of tiny pores. This enhancement not only accelerates the dissolution of electrode substances but also reduces the transmission routes of electrons and ions, thus boosting efficiency and laying a robust structural base for optimizing electrochemical efficiency.

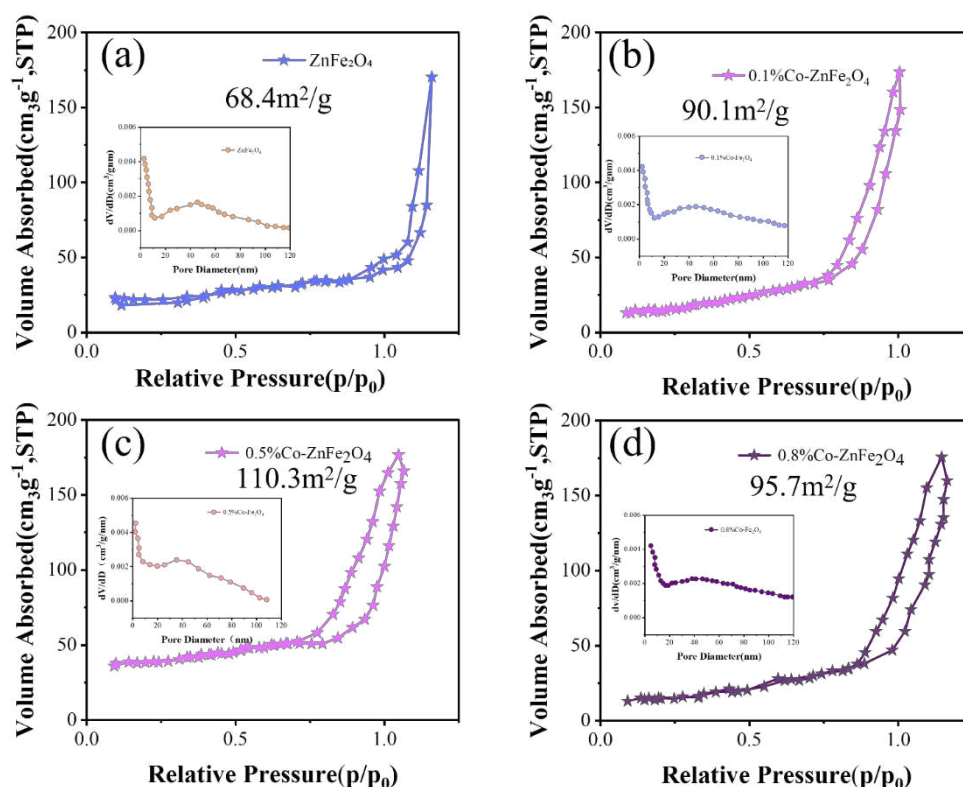


Fig. 12 N₂ adsorption-desorption isotherms and pore size distribution of ZnFe₂O₄, 0.1% Co-ZnFe₂O₄, 0.5% Co-ZnFe₂O₄ and 0.8% Co-ZnFe₂O₄

Following the performance evaluation of Ce-doped ZnFe₂O₄ substances, the electrochemical efficacy of Co-doped ZnFe₂O₄ was assessed. Fig. depicting its CV curve. Fig. 13 (a) displays a nearly rectangular capacitance pattern, with the most extensive curve at 12 hours; Fig. 13 (b) illustrates the most prolonged discharge duration in 12 hours, showcasing superior charge and discharge efficiency; Fig. 13 (c) attains a specific capacity of 426 at 12 hours F/g, significantly exceeding 4 hours (297 F/g), 8 hours (338 F/g), and 16 hours (371 F/g). The reason for this is the

incorporation of numerous active sites and crystal imperfections through Co doping, which enhances the material's porous nature and significantly boosts the electron and ion transfer rate in the electrolyte; as depicted in electrochemical impedance spectroscopy Fig. 13 (d), at 12 hours, the material exhibits the least high-frequency impedance and quickest ion diffusion rate. The electrochemical efficiency is enhanced due to Co doping's role in controlling ZnFe₂O₄'s electronic configuration and lowering the energy barrier for charge transfer.

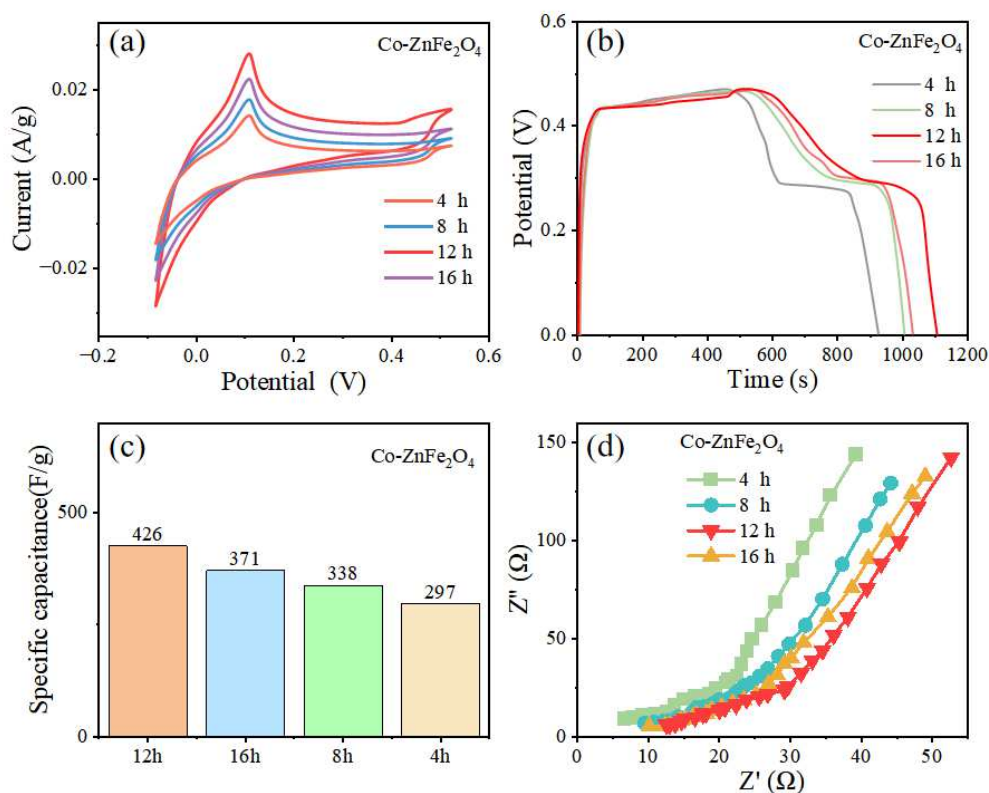


Fig. 13 (a) Cyclic voltammetry (CV) curves of Co-ZnFe₂O₄ at 2 hours, 8 hours, 12 hours and 16 hours; (b) Galvanostatic charge and discharge (GCD) curves of Co-ZnFe₂O₄ at 2 hours, 8 hours, 12 hours and 16 hours; (c) Co-ZnFe₂O₄ at 2 hours, 8 hours, 12 hours, 16 hours and a current density of 3 Specific capacity diagram at A/g; (d) Cycle performance diagram of Co-ZnFe₂O₄ nanowires at a current density of 1 A/g; (e) Impedance diagram of Co-ZnFe₂O₄ at 2 hours, 8 hours, 12 hours, and 16 hours.

This research investigated the effect of Co doping ratio on ZnFe₂O₄'s electrochemical characteristics via experiments on unadulterated ZnFe₂O₄ and 0.1%, 0.5%, 0.8% Co-ZnFe₂O₄ (Fig. 14). CV test (Fig. 14 (a)) showed that Co doping increased the CV curve area with rising doping levels, and all Co-doped samples had clear redox peaks/irregularities in -0.3V-0.2V (pseudocapacitive properties). GCD test (Fig. 14 (b), 4mV/s scanning) indicated 0.5% Co-ZnFe₂O₄ had the longest charge-discharge duration and best efficiency. At 3A/g current density, specific capacitances were: ZnFe₂O₄ 297F/g, 0.1% Co-ZnFe₂O₄ 332F/g, 0.5% Co-ZnFe₂O₄ 422F/g, 0.8%

Co-ZnFe₂O₄ 358F/g (Fig. 14 (c)), confirming 0.5% as the optimal Co doping ratio (peak specific capacitance). Co-ZnFe₂O₄ had a larger specific surface area than unadulterated ZnFe₂O₄, enhancing charge absorption and electrochemical performance. EIS test (Fig. 14(d), 5Hz-100Hz) showed 12-hour synthesized Co-ZnFe₂O₄ had a steep vertical low-frequency line (lower Warburg impedance, better capacitance) and reduced high-frequency semicircle (lower electron transfer resistance, better conductivity); 0.5% Co-ZnFe₂O₄'s capacitance was closest to an ideal supercapacitor, so it was selected as the test material.

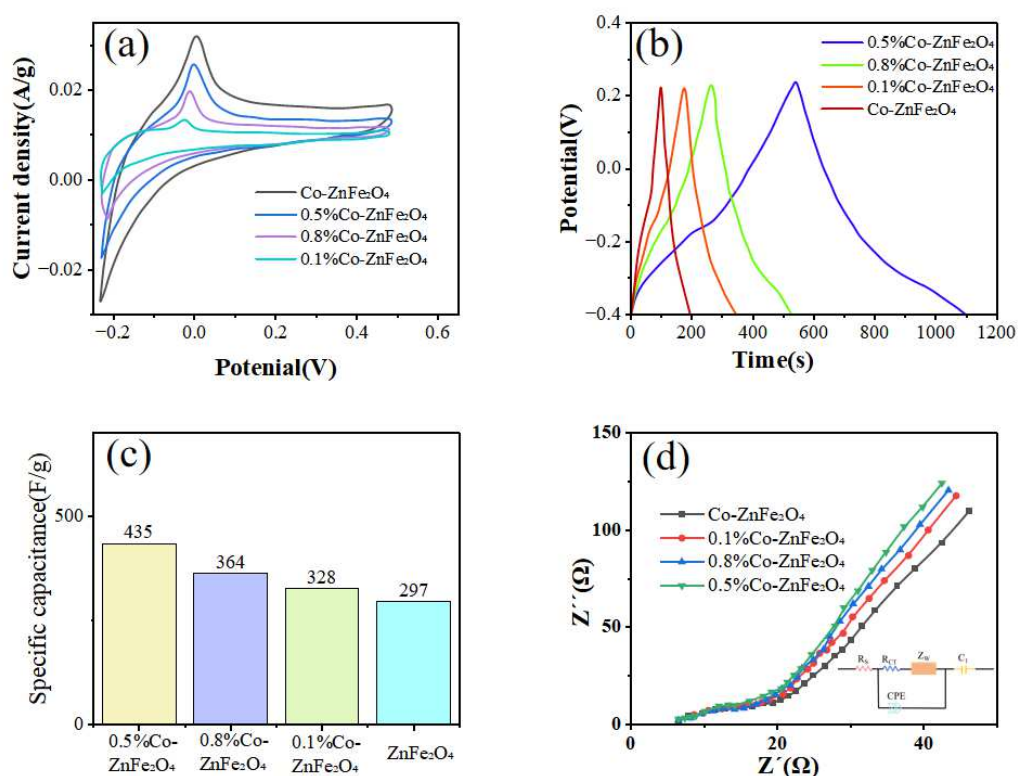


Fig. 14 (a) Cyclic voltammetry (CV) curves of ZnFe₂O₄, 0.1% Co-ZnFe₂O₄, 0.5% Co-ZnFe₂O₄ and 0.8% Co-ZnFe₂O₄; (b) ZnFe₂O₄, 0.1% Co-ZnFe₂O₄, 0.5% Galvanostatic charge-discharge (GCD) curves of Co-ZnFe₂O₄ and 0.8% Co-ZnFe₂O₄ at 4 mV/s; (c) ZnFe₂O₄, 0.1% Co-ZnFe₂O₄, 0.5% Co-ZnFe₂O₄ and 0.8% Co-ZnFe₂O₄ at a current density of 3 A/g; (d) Impedance diagram of ZnFe₂O₄, 0.1% Co-ZnFe₂O₄, 0.5% Co-ZnFe₂O₄ and 0.8% Co-ZnFe₂O₄.

An electrochemical workstation was used to analyze the Co-ZnFe₂O₄ electrode in KOH alkaline electrolyte, with a voltage range of -0.4V to 0.5V. Cyclic voltammetry (CV) curves were collected at scanning velocities of 5, 10, 20, 30, 50, and 80 mV/s (Fig. 15 (a)), all showing non-rectangular shapes with obvious redox peaks (a typical pseudocapacitive trait). As scanning speed increased from 5 to 80 mV/s, peak current increased linearly without significant distortion or peak shift, indicating excellent reaction kinetics, structural stability and stable electrochemical performance. Specific capacitance tests at the same scanning velocities (Fig. 15 (a)-(c)) yielded values of 248, 266, 297, 345, 389, and 448 F/g

sequentially, attributed to prolonged discharge time and enhanced electrode-electrolyte interaction at higher speeds. Additionally, linear fitting of $\log(i)$ and $\log(v)$ (Fig. 15) showed a strong correlation; the b values for anode and cathode were 0.77 and 0.83 respectively (near 1), indicating the material is mainly controlled by surface pseudocapacitance with supplementary diffusion control (Fig. 15(e)). At 10 mV/s (Fig. 15 (f)), the empirical equation $i = k_1 v + k_2 v^{1/2}$ was used to analyze dual control mechanisms: diffusion dominates at low scanning speeds, while pseudocapacitance control increases with speed, reaching 75% at 140 mV/s, confirming the material's pseudocapacitive dynamic properties.

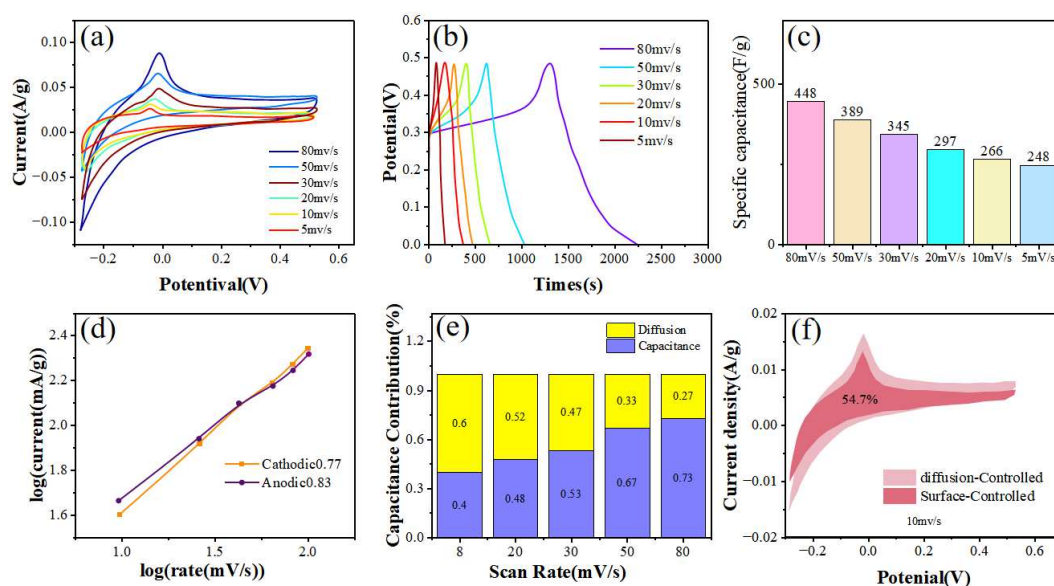


Fig. 15 (a) Cyclic voltammetry (CV) curves of Co-ZnFe₂O₄ at different scan rates; (b) Charge-discharge curves of Co-ZnFe₂O₄ nanorods at different current densities; (c) C under different current densities Specific capacity of o-ZnFe₂O₄ nanorods; (d) linear plot of logarithm (i) and logarithm (v); (e) contribution rate of pseudocapacitance at different scan rates; (f) current at 10mV/s is divided into surface control and diffusion control

5 Assessing the physical properties and electrochemical efficiency of Ce,Co-ZnFe₂O₄ nanosheet electrodes

Characterizing the distribution of elements is depicted in Fig. 16. Fig. 16(a) to (e) demonstrate that the synthesized Ce, Co-ZnFe₂O₄ substance comprises five components: Zn, Ce, O, Fe, and Co, each uniformly distributed within the ZnFe₂O₄ nanostructure, aligning closely with the material's general structural contour. The absence of clear areas for element enrichment or depletion verifies the material's high purity and the non-detection of other impurities.

This research employed an X-ray diffractometer (XRD) for in-depth examination of the sample's structural features, chemical composition, and element valence. Fig. 16 (f) displays the X-ray diffraction spectrum of ZnFe₂O₄, Ce-ZnFe₂O₄, Co-ZnFe₂O₄, and Ce,Co-ZnFe₂O₄ nanomaterials. The results revealed that double doping of Ce and Co did not cause obvious changes in the main crystal phase of the sample, but slight fluctuations in the intensity and morphology of some diffraction peaks were observed. This discovery verifies that incorporating Ce and Co plays a regulatory role in the crystal's lattice characteristics, grain dimensions, and crystallinity to some degree.

Introducing both Ce and Co elements can enhance the material's conductivity by providing extra carriers; furthermore, the material's nanoscale configuration may induce quantum confinement phenomena, influencing electron behavior. In electrochemical energy storage systems such as supercapacitors, these characteristics help boost ion storage and diffusion efficiency, as well as refine charge-discharge efficiency and cycle stability; in electronic devices, they markedly improve conductivity. Additionally, the addition of Ce and Co enhances the material's structural stability, enabling it to maintain steady performance under complex environmental conditions such as temperature changes and humidity fluctuations by adjusting doping concentrations and methods.

Fig. 16(g) illustrates a scanning electron microscopy (SEM) image of Ce,Co-ZnFe₂O₄ nanomaterials characterized by a hierarchical flower-like morphology. The results showed that at similar particle sizes, the double-doped compound possessed a larger specific surface area compared with the undoped sample. This feature facilitates electron migration and ion diffusion,

provides more active sites to amplify the catalytic effect, and promotes charge storage and transfer, thereby improving the electrochemical performance of the electrode material.

Analysis of the SEM images reveals that after Ce and Co double doping, the flower-like morphology of ZnFe_2O_4 is largely preserved, but obvious changes occur in its fine structure: the flower-like “petals” show slight distortion and deformation, losing part of their regularity compared with the undoped state; the surface of the “petals” becomes rougher, with increased defects and uneven protrusions and depressions. This phenomenon is ascribed to the incorporation of dopant atoms into the ZnFe_2O_4 lattice. Furthermore, after doping, the size distribution of the flower-like structures broadens, and slight aggregation within these floral assemblies can be observed, leading to the formation of larger aggregates.

Compared with single-doped Ce- ZnFe_2O_4 and Co- ZnFe_2O_4 samples, the double-doped Ce,Co- ZnFe_2O_4 exhibits a more stable porous flower-like structure, while the other doped samples show similar porous floral characteristics. The structural advantages of ZnFe_2O_4 enhance its structural robustness, allowing it to retain its flower-like and crystalline morphologies under harsh temperatures or conditions, thus extending its service life.

To further reveal the internal microstructure and crystal nature at the nanoscale, transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were employed. Fig. 16 (h) presents the TEM image of Ce,Co- ZnFe_2O_4 , which clearly displays the hierarchical flower-like assembly composed of ultrathin nanosheets, with a porous and interconnected texture consistent with the morphological features observed by

SEM. The uniform contrast in the TEM image indicates good crystallinity and homogeneous microstructure without obvious amorphous regions or severe lattice distortion.

Fig. 16(i) shows the HRTEM image of Ce,Co- ZnFe_2O_4 , where clear and ordered lattice fringes are visible, confirming the high crystallinity of the doped sample. The measured lattice spacing of 0.25 nm corresponds to the (311) crystal plane of the spinel ZnFe_2O_4 structure, which is consistent with the XRD results. The inset in Fig. 16(i) is the selected area electron diffraction (SAED) pattern, exhibiting a series of concentric diffraction rings, further verifying the polycrystalline nature of the as-synthesized Ce,Co- ZnFe_2O_4 and the retention of the main spinel phase after double doping. These TEM and HRTEM results strongly support the XRD and elemental mapping analysis, confirming the successful doping and stable crystal structure of the material.

After comprehensive analysis of SEM, TEM, HRTEM, XRD, and elemental mapping data, it is evident that dual doping of Ce and Co significantly modifies the microstructure and electrochemical properties of ZnFe_2O_4 . The doped material possesses an enlarged specific surface area, more abundant active sites, and superior electron transport properties, enhancing its efficiency and stability in electrochemical applications. Moreover, the uniform distribution of elements further confirms the effectiveness of the doping process and the high purity of the material.

The results of the above analysis provide important theoretical support and practical guidance for further optimizing material properties and expanding application fields.

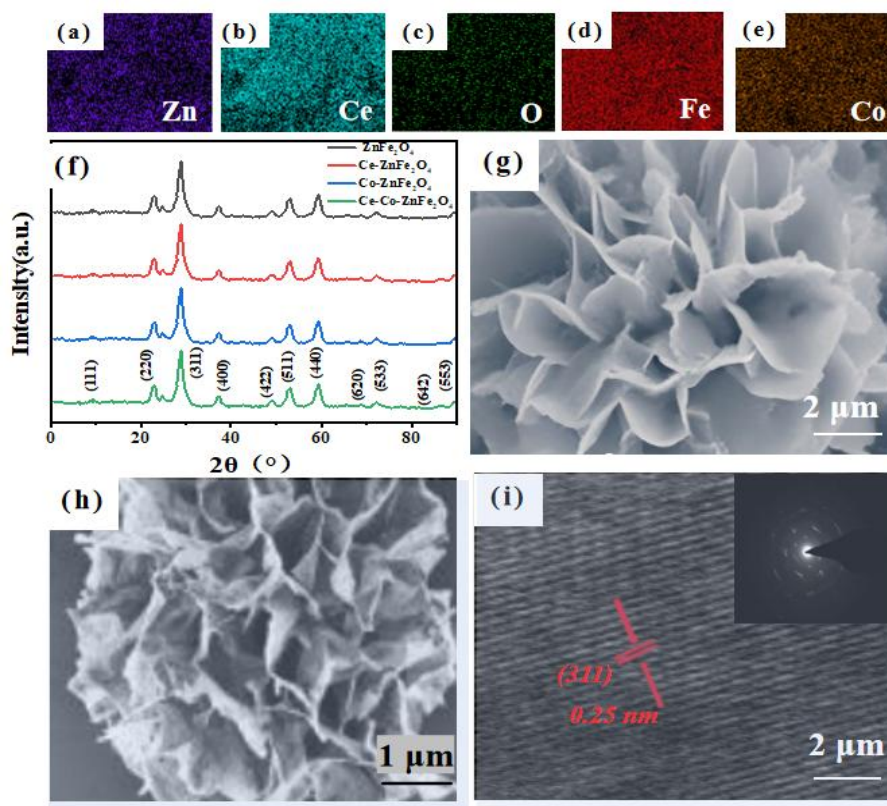


Fig. 16 Structural and morphological characterizations of Ce,Co-ZnFe₂O₄ nanomaterials:(a)–(e) EDS elemental mapping images of Zn, Ce, O, Fe, and Co, respectively;(f) XRD patterns of ZnFe₂O₄, Ce-ZnFe₂O₄, Co-ZnFe₂O₄, and Ce,Co-ZnFe₂O₄;(g) SEM image showing the hierarchical flower-like morphology;(h) TEM image of the as-synthesized sample;(i) HRTEM image (inset: selected area electron diffraction pattern)

To investigate the effect of Ce and Co co-doping on the oxygen defects in ZnFe₂O₄, O 1s XPS characterization was performed on both the pure and doped samples, as shown in Fig 17. As illustrated, the O 1s spectra can be deconvoluted into three characteristic peaks: hydroxyl oxygen at a binding energy of approximately 532.0 eV, oxygen vacancies at approximately 530.8 eV, and lattice oxygen at approximately 529.8 eV. The comparison reveals that the peak area of oxygen vacancies in Ce,Co-ZnFe₂O₄ is significantly

larger than that in pure ZnFe₂O₄, accompanied by a notably enhanced peak intensity, demonstrating that Ce and Co co-doping successfully introduces a large number of oxygen vacancies and effectively increases the oxygen vacancy concentration in the material. The increase in oxygen vacancies can promote electron transfer and oxygen species activation, providing a critical structural guarantee for the improvement of the catalytic and other application performances of the material (Fig 17.)

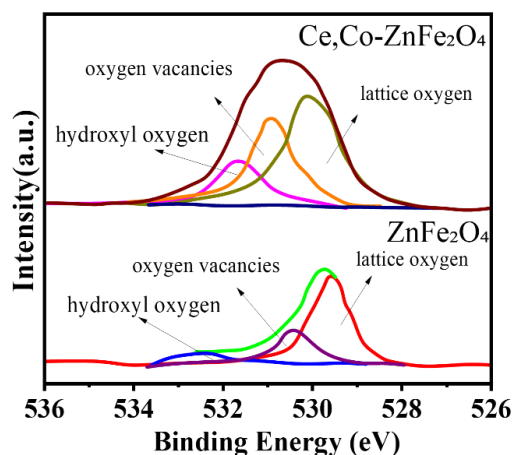


Fig. 17 Deconvoluted high-resolution O 1s XPS spectra of pure ZnFe_2O_4 and Ce,Co co-doped ZnFe_2O_4

In order to gain a deeper understanding of the impact of Ce and Co bimetallic doping on the electronic structure and defect chemical properties of ZnFe_2O_4 , we used X-ray photoelectron spectroscopy (XPS) technology to conduct a detailed chemical valence state analysis of the elements on the surface of the sample. Fig. 17 presents us the complete XPS spectrum of Ce,Co- ZnFe_2O_4 and the high-resolution spectrum of each element.

The results of the full spectrum (Fig. 18 a) prove that the material is composed of the elements Zn, Ce, Co, Fe, and O, which is consistent with our expected stoichiometric ratio. In the high-resolution Zn 2p spectrum (Fig. 18, In the Fe 2p spectrum (Fig. 18, e), the main peaks of $\text{Fe } 2p^{3/2}$ and $\text{Fe } 2p^{1/2}$ are distributed at 711.0 eV and 724.5 eV, which indicates that the iron element is mainly Fe^{3+} , which maintains the core structure of spinel. It is worth mentioning that both Ce and Co doping elements exhibit mixed valence state characteristics. In the Ce 3d spectrum (Fig. 18, c), the complex multimodal structure can be attributed to the co-existence of Ce^{3+} and Ce^{4+} . In the Co 2p spectrum (Fig. 18,), in addition to the main peaks (780.5 eV and 796.0 eV), the

accompanying strong satellite peaks further confirm the mixed valence state of Co^{2+} and Co^{3+} . It is worth noting that the high-resolution spectrum of O 1s (Fig. 18, f) provides conclusive experimental basis for the existence of oxygen vacancies. By peak fitting of the O1s spectrum, we can determine that convoluted is three significant characteristic peaks: lattice oxygen (O_{latt}) combined with metal) at approximately 529.8 eV, oxygen vacancies at approximately 531.5 eV, and surface adsorbed oxygen/hydroxyl oxygen (O_{ads}) at approximately 532.8 eV. The appearance of the oxygen vacancy characteristic peak clearly reveals that the successful doping of Ce,Co destroyed the original charge balance state of ZnFe_2O_4 , thus triggering the generation of a large number of oxygen vacancies. Normally, the relative concentration of oxygen vacancies can be estimated by the proportion of the oxygen vacancy peak area in the total O 1s peak area. Calculated data reveal that there is an obvious oxygen vacancy concentration in Ce,Co- ZnFe_2O_4 . This provides a core reference for our in-depth understanding of the electronic structure optimization and electrochemical properties enhancement of materials.

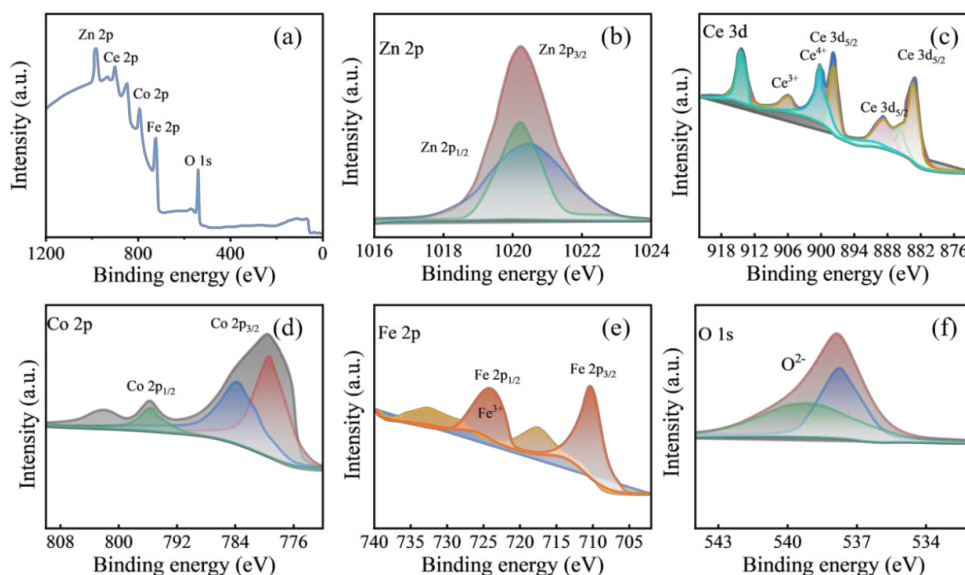


Fig. 18 (a) Ce,Co-ZnFe₂O₄ material; (b) Zn 2p XPS spectrum; (c) Ce 3d XPS spectrum; (d) Co 2p XPS spectrum; (e) Fe 2p XPS spectrum (f) O 1s XPS spectrum

Nitrogen adsorption-desorption tests were conducted to investigate the BET specific surface area and pore size distribution of pure ZnFe₂O₄ and Ce,Co co-doped ZnFe₂O₄ (Ce,Co-ZnFe₂O₄). The test results are shown in Fig 19 (a)-(d) (corresponding to the isotherms and pore size diagrams of the four materials). All four materials exhibit standard type IV adsorption-desorption isotherms and H3-type hysteresis loops, confirming their mesoporous nature; the distinct hysteresis loop of pure ZnFe₂O₄ appears in the relative pressure range of 1.0-1.2, while that of 0.5% Ce,Co-ZnFe₂O₄ emerges at a relative pressure of approximately 0.7, indicating that Ce and Co co-doping can promote the early formation of pores in the material nanosheets and increase their quantity. BET analysis shows that the specific surface areas of pure ZnFe₂O₄, 0.1% Ce,Co-ZnFe₂O₄, 0.5% Ce,Co-ZnFe₂O₄, and 0.8% Ce,Co-ZnFe₂O₄ are 68.4 m²/g, 98.2 m²/g, 126.4 m²/g, and 105.1 m²/g, respectively, confirming that Ce,Co co-doping can increase the specific

surface area of ZnFe₂O₄, thereby enhancing the electrochemical reaction activity and accelerating the migration of electrolyte ions. The pore size distribution curves indicate that the main pore diameters of the four materials are approximately 29 nm, 32 nm, 35 nm, and 33 nm, respectively, which is consistent with the conclusion of the mesoporous structure; in addition, a distinct characteristic peak appears at 7 nm for 0.5% Ce,Co-ZnFe₂O₄, indicating a significant increase in the number of small pores, which can inhibit excessive grain growth and further increase the specific surface area. In summary, Ce and Co co-doping provides sufficient active sites for electrochemical reactions by increasing the specific surface area and the number of small pores, while improving the wettability rate of electrode materials in the electrolyte, shortening the electron and ion transfer paths, and laying a solid structural foundation for optimizing the electrochemical performance of the material.

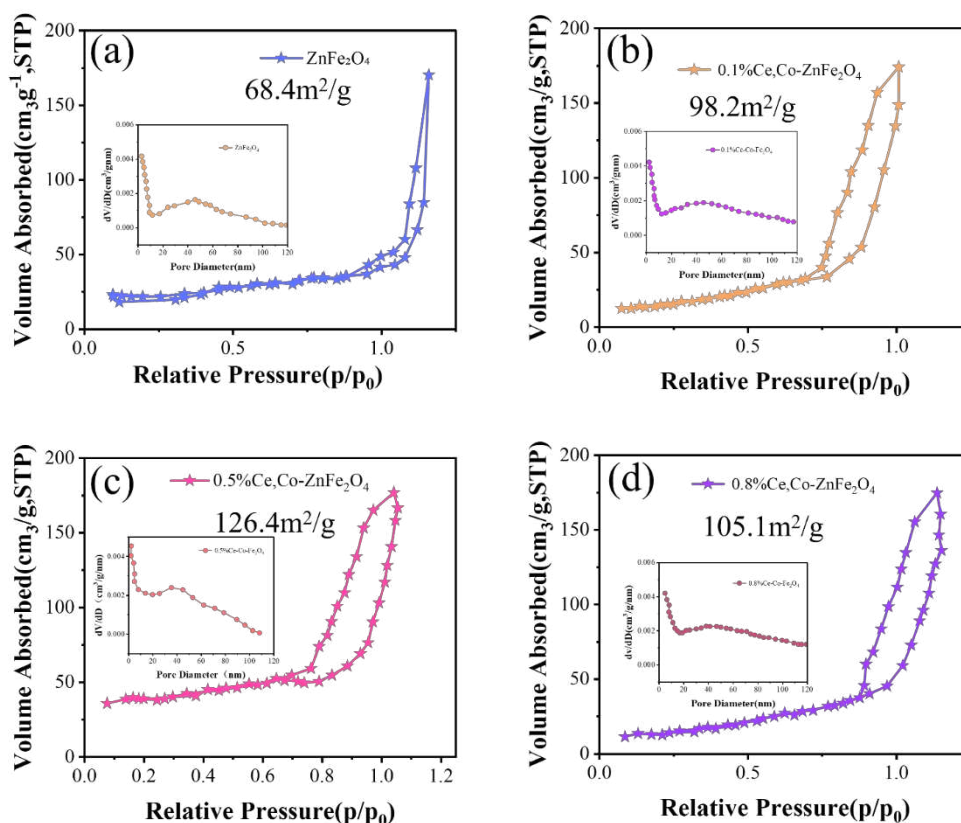


Fig. 19 N_2 adsorption-desorption isotherms and pore size distribution of ZnFe_2O_4 , 0.1% Ce, Co- ZnFe_2O_4 , 0.5% Ce, Co- ZnFe_2O_4 and 0.8% Ce, Co- ZnFe_2O_4

After infusing both Ce and Co into ZnFe_2O_4 and testing its electrochemical performance, the CV curve (Fig 20 a) exhibits standard rectangular capacitance features. The charge and discharge curve (Fig 20 b) and specific capacity histogram (Fig 20 c) show that the sample prepared for 12 hours has the longest discharge duration, superior charge and discharge efficiency, and a specific capacity of 504 F/g —markedly surpassing those of 4 hours (397 F/g), 8 hours (442 F/g), and 16 hours (479 F/g), and higher than that of the two single-doped ZnFe_2O_4 samples. Ce and Co dual

doping creates abundant active sites and crystal defects, improves the material's porous quality, and accelerates electron and ion transfer. The electrochemical impedance spectrum (Fig 20 d) indicates the 12-hour sample has minimal high-frequency resistance and the fastest ion diffusion rate, attributed to the double doping adjusting ZnFe_2O_4 's electronic configuration and reducing charge transfer energy barriers, thus achieving optimal electrochemical properties at the 12-hour preparation stage.

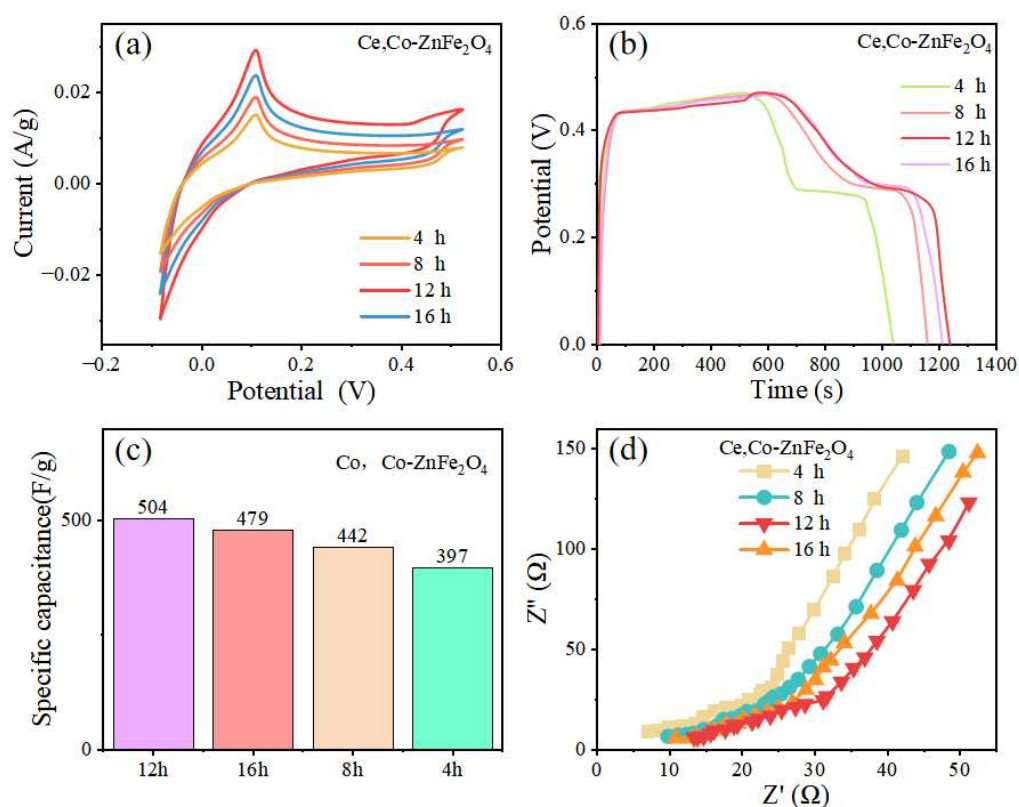


Fig. 20 (a) Cyclic voltammetry (CV) curves of Ce,Co-ZnFe₂O₄ at 2 hours, 8 hours, 12 hours and 16 hours; (b) Ce,Co-ZnFe₂O₄ at 2 hours, galvanostatic charge and discharge (GCD) curves at 8 hours, 12 hours and 16 hours; (c) Ce,Co-ZnFe₂O₄ at 2 hours, 8 hours, 12 hours, 16 hours and the current density is 3 Specific capacity diagram at A/g; (d) Impedance diagram of Ce,Co-ZnFe₂O₄ at 2 hours, 8 hours, 12 hours, and 16 hours

This study explored the impact of Ce-Co co-doping ratio on ZnFe₂O₄'s electrochemical properties via tests on pure ZnFe₂O₄ and 0.1%, 0.5%, 0.8% Ce-Co-ZnFe₂O₄ (Fig 21). CV test (Fig. 21(a)) showed that increasing Ce-Co co-doping enlarged the CV curve area; all co-doped samples had clear redox peaks/bulges in 0.1V-0.4V (pseudocapacitance traits). GCD test (Fig 21(b), 4mV/s scanning) confirmed 0.5% Ce-Co-ZnFe₂O₄ had the longest charge-discharge duration and best efficacy. At 3A/g current density, specific capacitances were: pure ZnFe₂O₄ 297F/g, 0.1% Ce-Co-ZnFe₂O₄ 424F/g, 0.5% Ce-Co-ZnFe₂O₄ 511F/g, 0.8% Ce-Co-ZnFe₂O₄

478F/g (Fig 21(c)), confirming 0.5% as the optimal co-doping ratio (peak specific capacitance). Ce-Co-ZnFe₂O₄ had a larger specific surface area than pure ZnFe₂O₄, enhancing charge absorption and electrochemical performance. EIS test (Fig 21(d), 5Hz-100Hz) showed 12-hour synthesized Ce-Co-ZnFe₂O₄ had a steep vertical low-frequency line (minimal Warburg impedance, superior capacitance) and reduced high-frequency semicircle (minimal electron transfer resistance, better conductivity); 0.5% Ce-Co-ZnFe₂O₄'s capacitance was closest to an ideal supercapacitor, so it was selected as the test subject.

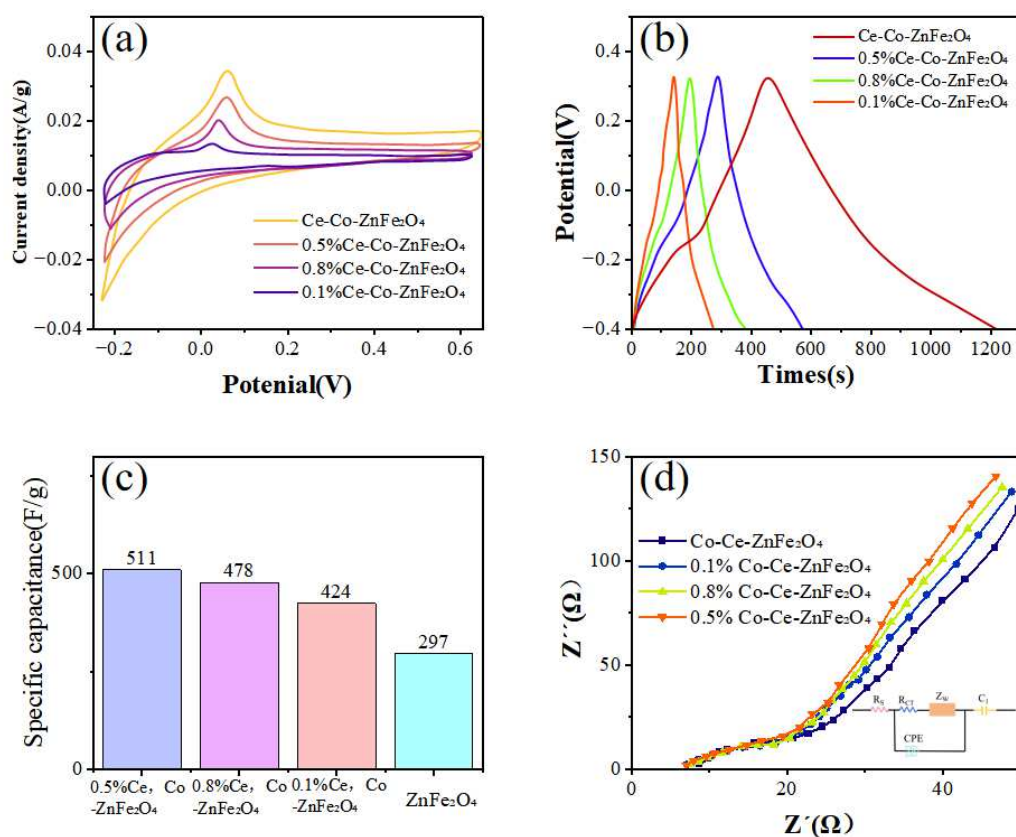


Fig. 21 (a) Cyclic voltammetry (CV) curves of ZnFe₂O₄, 0.1% Ce, Co-ZnFe₂O₄, 0.5% Ce, Co-ZnFe₂O₄ and 0.8% Ce, Co-ZnFe₂O₄; (b) ZnFe₂O₄, 0.1% Galvanostatic charge and discharge (GCD) curves of Ce, Co-ZnFe₂O₄, 0.5% Ce, Co-ZnFe₂O₄ and 0.8% Ce, Co-ZnFe₂O₄ at 4 mV/s; (c) ZnFe₂O₄, 0.1% Ce, Co-ZnFe₂O₄, 0.5% Specific capacity diagram of Ce, Co-ZnFe₂O₄ and 0.8% Ce, Co-ZnFe₂O₄ at a current density of 3 A/g; (d) ZnFe₂O₄, 0.1% Ce, Co-ZnFe₂O₄, 0.5% Ce, Co-ZnFe₂O₄ and ZnFe₂O₄ 0.8% Impedance diagram of Ce, Co-ZnFe₂O₄

An electrochemical workstation was employed to conduct electrochemical tests on the Ce, Co-ZnFe₂O₄ electrode in KOH alkaline electrolyte, with a voltage range of -0.4V to 0.5V. Cyclic voltammetry (CV) curves were collected at scanning velocities of 5, 10, 20, 30, 50, and 80 mV/s (Fig 22 (a)), all showing nearly non-rectangular shapes with distinct redox peaks, which confirms its pseudocapacitive charge storage capability. As scanning speed increased from 5 to 80 mV/s, peak current rose linearly without noticeable distortion or peak shift, indicating excellent electrochemical reaction speed, structural robustness, and stable electrochemical efficiency. Capacitance tests at the same scanning rates (Fig 22 (a)-(c)) yielded

specific capacitance values of 403, 429, 449, 465, 486, and 517 F/g sequentially, which is related to extended discharge duration, enhanced active material reactivity, and adequate electrode-electrolyte contact at higher speeds. Linear fitting of $\log(i)$ and $\log(v)$ (Fig 22 (d)) showed a strong correlation; the b values for anode and cathode were 0.78 and 0.82 respectively (approaching 1), indicating the material is mainly controlled by surface pseudocapacitance with diffusion control as a supplement (Fig 22 (e)). At 10 mV/s (Fig 22 (f)), the empirical equation $i = k_1 v + k_2 v^{1/2}$ revealed that diffusion dominates at low scanning speeds, while pseudocapacitance control increases with speed, reaching 75% at 140 mV/s, verifying the material's pseudocapacitive dynamic properties.

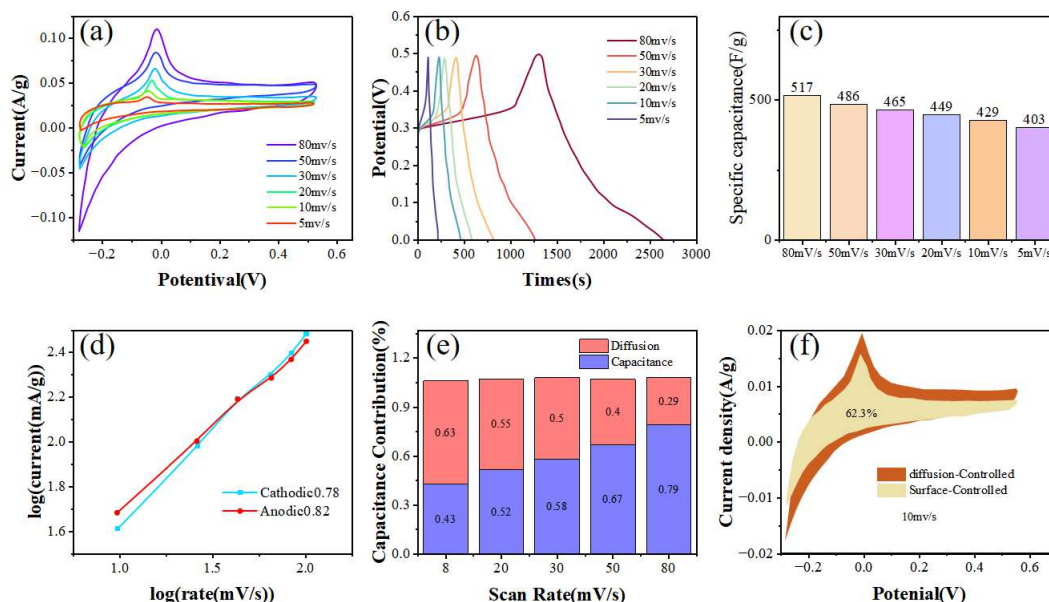


Fig. 22 (a) Cyclic voltammetry (CV) curves of Ce,Co-ZnFe₂O₄ at different scan rates; (b) Charge and discharge curves of Ce,Co-ZnFe₂O₄ nanorods at different current densities; (c) Under different current densities Specific capacity of Ce,Co-ZnFe₂O₄ nanorods; (d) Linear graph of logarithm (i) and logarithm (v); (e) Contribution rate of pseudocapacitance at different scan rates; (f) Current at 10 mV/s is divided into surface control and diffusion control

Fig 23 (a), (b), and (c) display the results of charge-discharge cycle tests on Ce-ZnFe₂O₄, Co-ZnFe₂O₄, and Ce,Co-ZnFe₂O₄ electrode materials, respectively, at a current density of 1 A/g. All three materials exhibit excellent high-current charge-discharge capabilities and can maintain a high specific capacity even at an intense current density of 20 A/g. After 100 alternating charge-discharge cycles and 600 cycles at different current densities, when the current density is restored to 1 A/g, all materials can maintain high specific capacity and cycle stability: Ce-ZnFe₂O₄ has an initial specific capacity of 437 F/g, which remains 388 F/g after cycling, with a capacity retention rate of 88.7%. The improvement in its electrochemical performance stems from Ce element doping, which significantly increases the specific surface area of the material, forms additional active sites on the surface of the nanorods, improves electrical conductivity, and generates oxygen vacancies, thereby promoting

redox reactions. Co-ZnFe₂O₄ has an initial specific capacity of 448 F/g, which remains 387 F/g after cycling, with a capacity retention rate of 86%. The introduction of Co element can expand the specific surface area of the material, increase active sites on the surface of the nanorods, optimize the electronic structure, and enhance the adsorption capacity of reaction intermediates, promoting the full progress of redox reactions. Ce,Co-ZnFe₂O₄ shows the best performance, with an initial specific capacity as high as 517 F/g, which remains 471 F/g after cycling, and a capacity retention rate of 91%. The combined doping of Ce and Co not only expands the specific surface area of the material and forms additional active regions within the nanorod structure, but also improves reaction kinetics through precise modification of the electronic structure, ensuring the complete progress of redox reactions and thus achieving a significant improvement in specific capacity.

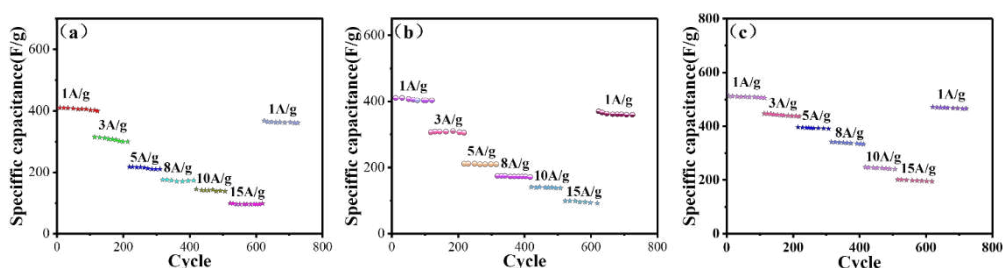


Fig. 23 Rate and cycle performance of Ce,Co-ZnFe₂O₄ nanorods under different current densities

Fig 24 illustrates the energy storage mechanism of ZnFe₂O₄-based electrode materials under the photoelectric synergistic effect. At the electrolyte–electrode interface, OH[−] ions undergo adsorption and desorption on the electrode surface, accompanied by interfacial charge separation corresponding to the electric double-layer capacitance behavior. Subsequently, the insertion/extraction of OH[−] triggers reversible surface redox reactions, accompanied by the reversible valence conversion between Fe²⁺ and Fe³⁺, which can be described by the following reaction: $\text{ZnFe}_2\text{O}_4 + x\text{OH}^- \rightleftharpoons \text{ZnFe}_2\text{O}_4(\text{OH})_x + x\text{e}^-$. Under light irradiation, photo-generated electron–hole pairs are efficiently generated within Ce,Co-doped ZnFe₂O₄. The doped metal sites act as charge traps to promote the separation and

migration of photo-induced charge carriers, effectively suppressing their recombination. The photogenerated electrons and holes participate synchronously in the surface redox reactions of Fe²⁺/Fe³⁺, providing extra charge carriers and accelerating the redox kinetics. Such a process couples the interfacial charge separation of electric double-layer capacitance and the reversible Faradaic redox behavior of pseudocapacitance. Meanwhile, the photoresponse process and electrochemical process are strongly coupled: the photoexcited carriers reduce the reaction activation energy and enhance charge transfer efficiency, which constitutes the key mechanism responsible for the superior rapid and reversible energy storage performance.

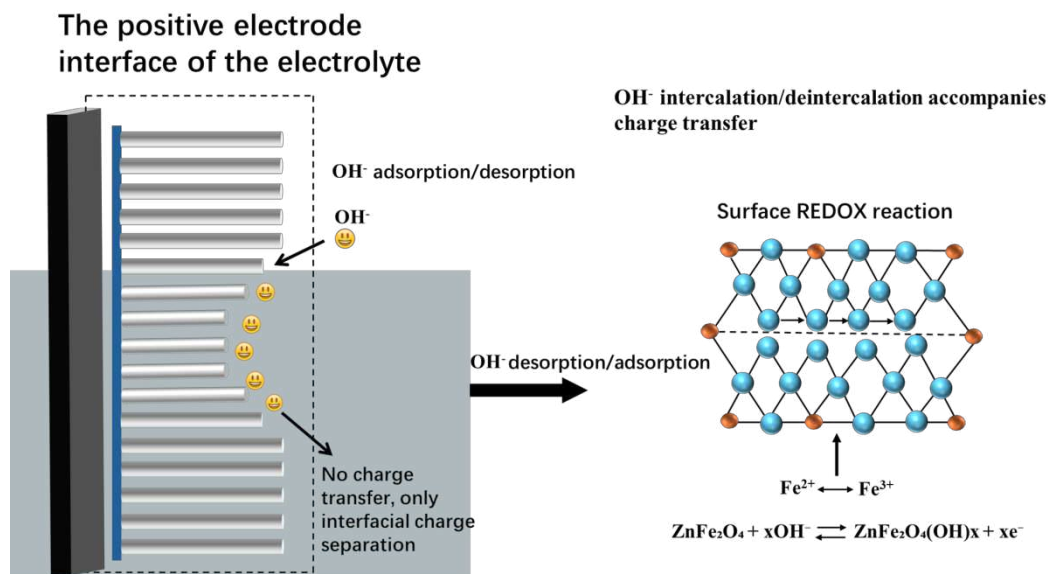


Fig. 24 Positive electrode reaction mechanism diagram

6. Negative electrode (CNTs) characterization

Following an in-depth examination of the electrochemical characteristics of carbon nanotubes, the CV curve Fig. was noted. Fig 25 (a) demonstrates a nearly rectangular shape symmetry across various scanning speeds, confirming its superior electrochemical reversibility; this symmetry is evident in the charge and discharge curve Fig 25 (b), along with the variations in discharge duration, all showcase its superior rate-matching capabilities; also, the capacity Fig. Under the 1 A/g scenario, Fig 25 (c) reaches a peak of 753. In contrast to F/g, its capacity remains substantially high even with rising current density, showcasing its superior rate efficiency. Post a Fig 25 (d) cycle stability assessment, this capacity stabilizes irrespective of the current density, indicating its outstanding

cycle performance. These performances are notably successful due to the combined effects of carbon nanotubes' enhanced conductivity, large specific surface area, and hollow tubular structure. Here, high conductivity accelerates electron transfer, a significant specific surface area provides numerous active sites, and the hollow structure facilitates rapid ion diffusion. Simultaneously, the solid stability of this framework diminishes its vulnerability to disintegration during the cycling cycle. Ultimately, carbon nanotubes are notable for their enhanced ability to store charges, their exceptional rate adaptability, and their prolonged stability in the cycle for electrochemical energy storage.

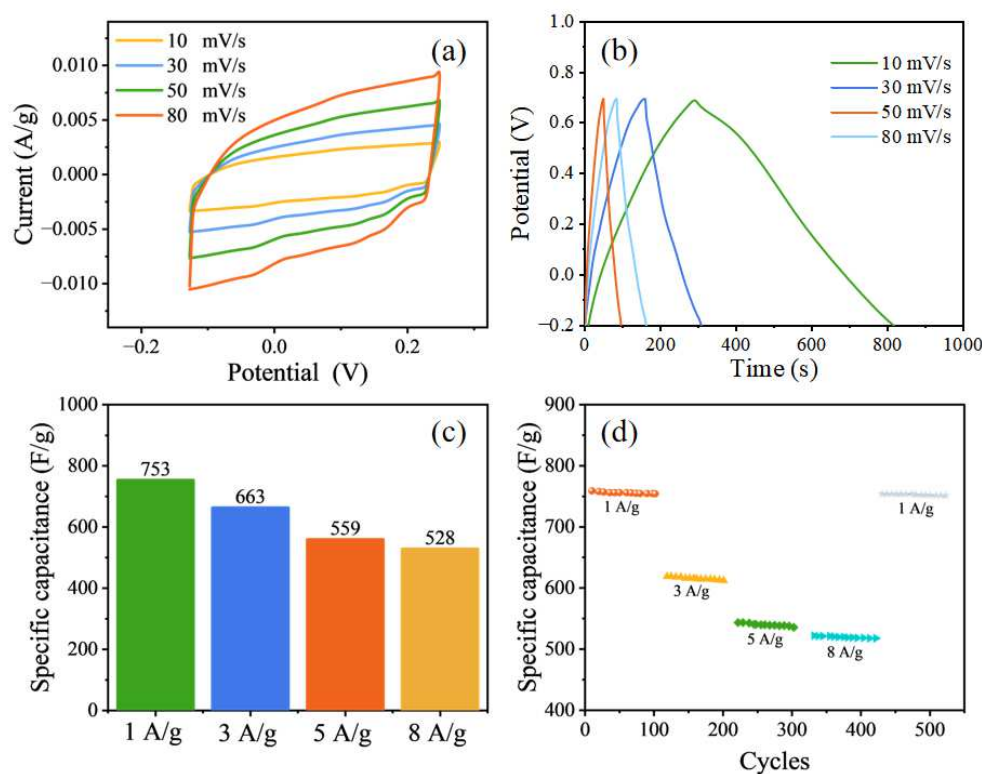


Fig. 25 (a) CV curves of carbon nanotubes at different scan rates; (b) Charge and discharge curves of carbon nanotubes at different current densities; (c) Specific capacity histograms of carbon nanotubes at different current densities; (d) Cycling stability curves of carbon nanotubes at different current density

7. Construction of asymmetric supercapacitor

First, accurately weigh the $\text{Ce,Co-ZnFe}_2\text{O}_4$ active material with the optimal doping ratio of 0.5%, conductive carbon black (Super P), and polyvinylidene fluoride (PVDF). The mass ratio of the three components is strictly controlled at 8:1:1. This ratio has been optimized repeatedly to minimize the electrode contact resistance, avoid masking the intrinsic capacitive properties of the active material caused by excessive conductive agent, and ensure that the measured capacitance truly reflects the electrochemical performance of $\text{Ce,Co-ZnFe}_2\text{O}_4$. Subsequently, add N-methylpyrrolidone (NMP) solvent dropwise to the mixed powder, and stir continuously at 300 r/min on a magnetic stirrer for 24 hours until a uniform, viscous electrode slurry without particle agglomeration is formed. The slurry viscosity is controlled within 500–800 mPa·s to guarantee uniform coating.

The above slurry is uniformly coated onto the surface of pretreated carbon cloth using an automatic film applicator. The carbon cloth is pretreated by ultrasonic cleaning in 1 mol/L H_2SO_4 for 30 minutes, rinsed with deionized water to neutrality, and then vacuum-dried at 100 °C for 12 hours to remove surface impurities and moisture and improve the adhesion between the

slurry and carbon cloth. The coating thickness is strictly controlled at 150 μm , and the advancing speed of the film applicator is maintained at 5 mm/s during coating to ensure uniform electrode thickness. After coating, the electrode is dried in a vacuum drying oven at 100 °C under 0.08 MPa vacuum for 12 hours to completely remove NMP solvent from the slurry, avoiding the influence of residual solvent on electrochemical performance tests. After drying, the electrode mass is weighed using an electronic balance with an accuracy of 0.1 mg. The mass loading of the active material is calculated by subtracting the mass of the blank carbon cloth from the mass of the coated electrode. Through repeated preparation and weighing, the active material mass loading of each electrode is precisely controlled at $1.0 \pm 0.05 \text{ mg/cm}^2$. As a key parameter for specific capacitance calculation, this control accuracy effectively eliminates calculation errors caused by loading deviation and ensures the reliability of the 517 F/g specific capacitance value. Finally, a $\text{Ce,Co-ZnFe}_2\text{O}_4$ positive electrode with a geometric area of 1 cm^2 , smooth surface, and no peeling is obtained. For the specific structure of the supercapacitor, please refer to Fig 26 below.

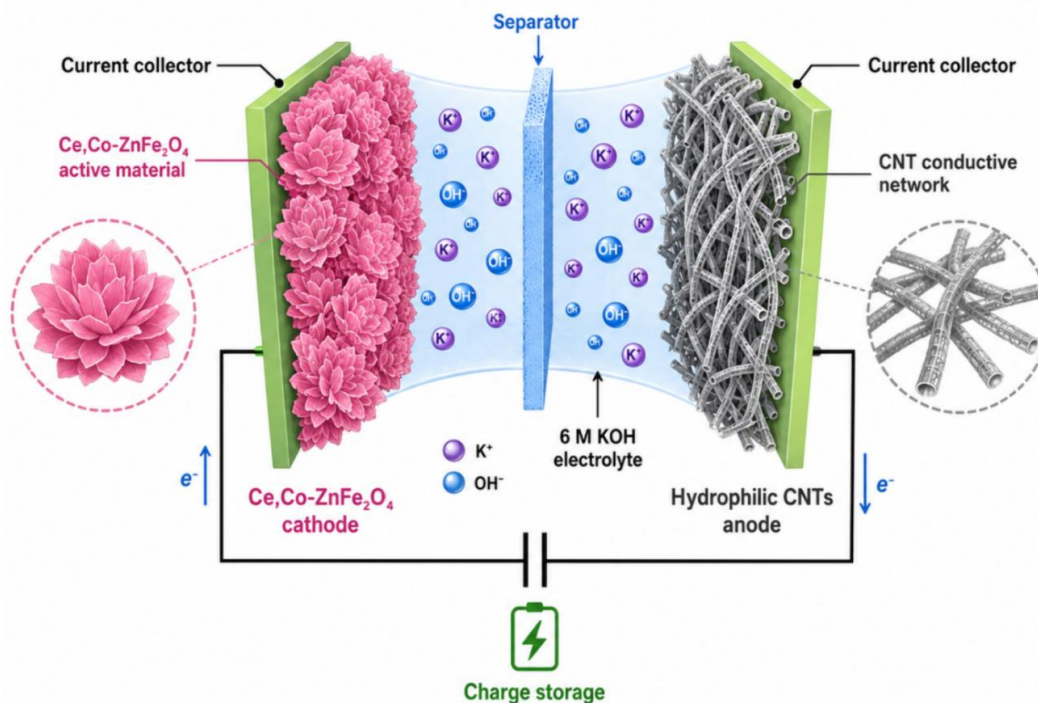


Fig. 26 Supercapacitor schematic diagram

Investigating the electrochemical properties of the Co-Ce double-doped ZnFe_2O_4 //CNTs supercapacitor revealed its coefficient of variation curve, as depicted in the Fig 27 (a-c) demonstrates consistent capacitance traits across a broad spectrum of voltages and varying scanning velocities. The primary reason for this is the combined impact of Co and Ce double doping with CNTs: The introduction of Co and Ce double doping leads to numerous active sites (like crystal flaws and heteroatom doping sites), altering ZnFe_2O_4 's electronic configuration (for instance, by refining energy bands and enhancing conductivity), thus markedly improving the electrode's electrochemical function and ion/electron transmission rate; CNTs leverage their exceptionally high conductivity and extensive specific surface area to construct an unbroken conductive network. This network not only expands the charge storage interface but also hastens the charge transfer rate and expands the area for energy storage. Fig 27 d) illustrates the charge-discharge curve's notable symmetry, underscoring its superior electrochemical reversibility. This is achieved by double doping, enhancing the redox reaction reversibility of ZnFe_2O_4 , and using CNTs to maintain electrode

interface structure stability throughout cycling, as detailed in the specific capacity test depicted in Fig 27 (e) illustrates that in varying current density scenarios, the apparatus sustains a considerable specific capacity while experiencing a slower decay rate. This is attributed to double doping boosting ZnFe_2O_4 's rate adaptability, and the CNTs conductive network's ability to effectively transmit charges and reduce resistive polarization under high current conditions, as depicted in the Fig 27. In Fig 27 (f), there has been a notable enhancement in the stability of cycling. The use of double doping improves the structural integrity of ZnFe_2O_4 , while the robust mechanical properties of CNTs decelerate the electrode's volume alteration and structural breakdown during its cycling process. Collectively, the advantages of this supercapacitor lie in its dual synergistic approach, combining "double-doped active site proliferation and electronic structure optimization" with "CNTs conductive network construction and specific surface area expansion", demonstrating consistent capacitance across a broad voltage range, elevated specific capacity, superior rate efficiency, and extended cycle steadiness.

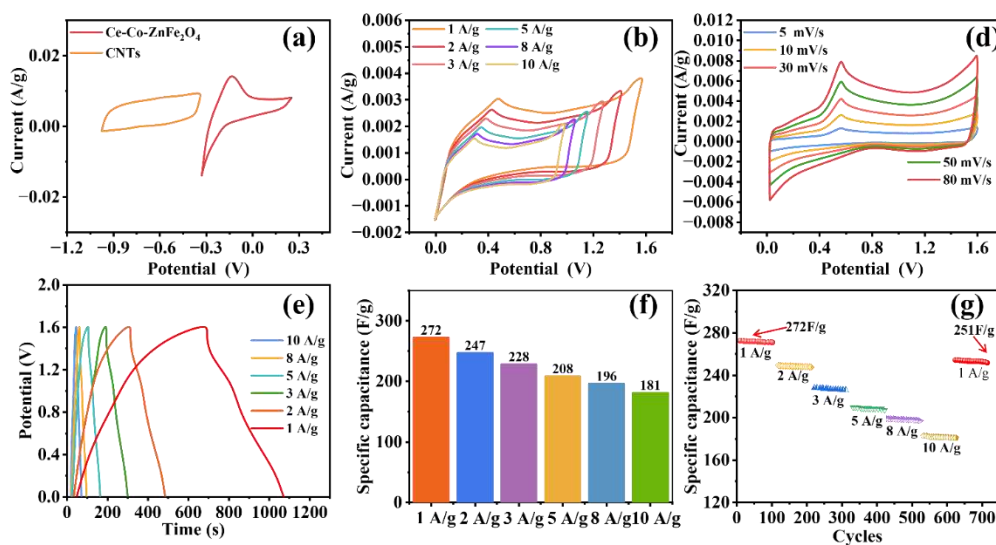


Fig. 27 (a) In three-electrode cell, scan rate is 4mV/s, 2M Cyclic voltammetry (CV) curves of Ce,Co-ZnFe₂O₄//CNTs electrode and CNTs in KOH electrolyte; (b) Cyclic voltammetry curves of Ce,Co-ZnFe₂O₄//CNTs at different scan rates; (c) Ce,Co-ZnFe₂O₄//CNTs at different current densities The charge and discharge curves; (d) The charge and discharge curves at different potentials when the current density is 4A/g; (e) The specific capacity diagram of Ce,Co-ZnFe₂O₄//CNTs at different scan rates; (f) The cyclic energy storage situation of the Ce,Co-ZnFe₂O₄//CNTs device when the current density is 3A/g.

Fig 28 (a) displays the outcomes of the cyclic stability tests conducted on the Ce,Co-ZnFe₂O₄//CNTs supercapacitor. The data indicates that following 10,000 cycles, there's a stabilization in the specific capacity from the starting 272 F/g to 251 F/g, with a capacitance retention rate reaching up to 85%. Fig 28 (b) illustrates the device's energy density as 12.5 Wh/Kg and its power density as 536 W/kg. In contrast to comparable supercapacitor devices, this one demonstrates an improved equilibrium between energy and power densities. Compared with state-of-the-art ZnFe₂O₄-based supercapacitors reported in recent literature, the Ce,Co-ZnFe₂O₄//CNTs device in this study shows significant advantages. Specifically, The cycle stability (85% retention after 10000 cycles) also outperforms the above two single-doped systems (83.2% after 7000 cycles and 86.1% after 5000 cycles, respectively). More importantly, this study is the first to integrate Ce,Co co-doping with photoelectric synergistic charging, enabling a 7.2% increase in specific capacity compared to pure electric charging—a function not reported in previous single-doped ZnFe₂O₄ electrodes. This improvement benefits from the synergistic effect of Ce,Co co-doping (introducing more oxygen vacancies and active sites) and the conductive

network of hydrophilic CNTs, which jointly promote charge transfer and ion diffusion. The remarkable efficiency achieved can be attributed to the combined impact of Co-Ce double doping and CNTs: while double doping adds numerous active sites to ZnFe₂O₄, improving pseudocapacitance storage, it simultaneously modifies the electronic configuration to boost conductivity, thus hastening charge transfer; CNTs, with their extensive specific surface area, enlarge the energy storage area at the interface and construct a highly conductive network, guaranteeing efficient power generation. The remarkable success of these performances stems from the synergistic impact of carbon nanotubes, characterized by their increased conductivity, expansive specific surface area, and a hollow tubular configuration. Here, high conductivity hastens electron movement, a significant specific surface area offers multiple active sites, and the hollow design aids in swift ion diffusion. Concurrently, the robust stability of this structure reduces its susceptibility to breakdown throughout the cycling process. Carbon nanotubes stand out for their superior charge storage capacity, remarkable rate flexibility, and extended stability throughout the electrochemical energy storage cycle.

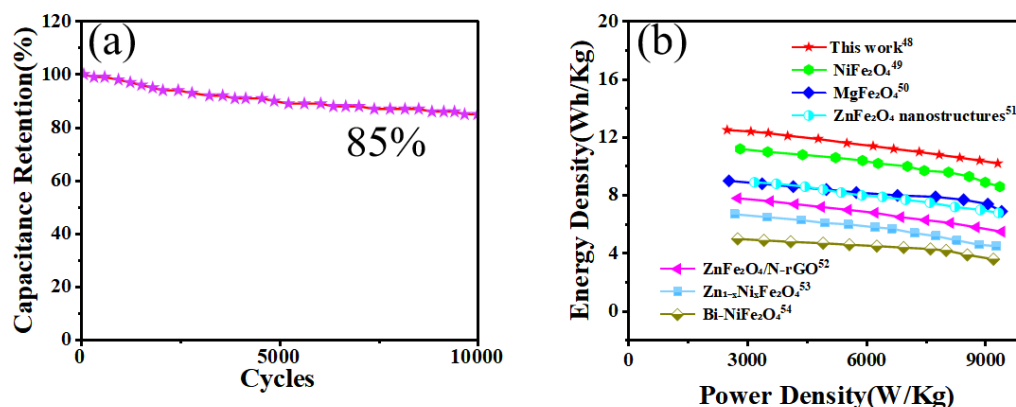


Fig. 28 (a) Cycling stability curve of Ce,Co-ZnFe₂O₄//CNTs supercapacitor; (b) Energy density-power density (Ragone) of different supercapacitor devices[48-54]

To further investigate the electrochemical stability during long-term cycling, EIS was conducted before and after 5000,10000 consecutive cycles. As displayed in Fig 29 , the charge transfer resistance after long-term cycling exhibits a slight

increase/decrease , suggesting the excellent structural and interfacial stability of the electrode during repeated charge/discharge processes.

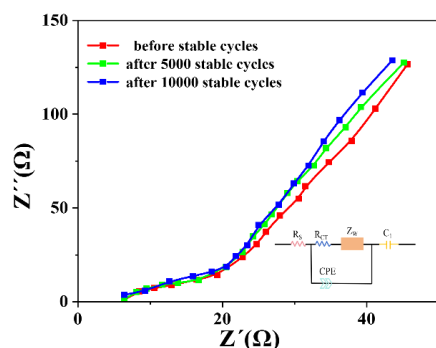


Fig. 29 EIS after 5,000/10,000 stable cycles

8 Research on photoelectric properties of Ce,Co-ZnFe₂O₄

Fig. 30 (a, b) illustrates the coefficient of variation (CV) for Ce,Co-ZnFe₂O₄/CNTs supercapacitor across various scanning speeds. The semi-rectangular shape displays a significant redox peak, indicating that the supercapacitor's energy storage mechanism has features of both dual-layer capacitance and pseudocapacitance. Pseudocapacitance arises due to the charge retention in the reversible redox reaction. The dual-layered capacitance guarantees rapid reaction and substantial power generation, while the pseudocapacitance enhances the device's capacity and energy concentration. Concurrently, with an identical scanning speed, the CV curve's coverage area for photoelectric collaborative charging exceeds that of the sole charging scenario, verifying the supercapacitor's ability to achieve greater specific capacity[55]. Fig. 30 (c,

d) displays the outcomes of analyzing the rate of capacitance contribution. The supercapacitor's capacitance configuration, be it through electrical or photoelectric co-charging, consists of both pseudocapacitance and diffusion (electric double layer) capacitance. Keeping the sweep rate constant leads to pseudocapacitance regularly exceeding diffusion capacitance in affecting results, suggesting that charge storage is mainly controlled by reversible redox reactions. Additionally, in the field of photoelectric collaborative charging, the contribution rate of pseudocapacitance significantly surpasses that of purely electrical charging. The main cause lies in the fact that during photoelectric collaborative charging, some of the light energy converts into electrical energy used for storage.

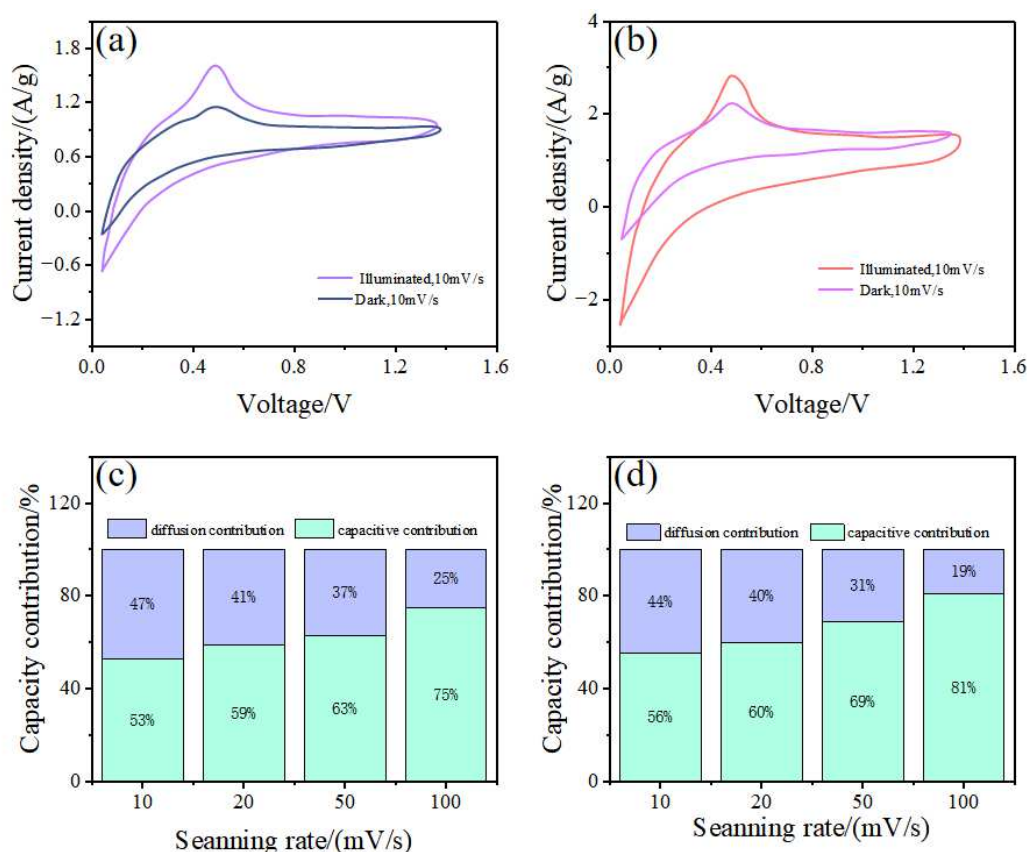


Fig. 30 (a, b) CV curves of supercapacitor at different scan rates, (c) capacitance contribution rate of electrical charging, (d) capacitance contribution rate of photoelectric collaborative charging

Ce,Co-ZnFe₂O₄, when used as a semiconductor, exhibits a valence band potential of 1.05 eV and a conduction band potential of -0.85 eV. Given its position in the conduction band, it functions as the photoanode (positive electrode) in a supercapacitor, whereas CNTs with a potential of -1.0~1.0 V are appropriate for the capacitor's cathode (positive electrode). The Ce,Co-ZnFe₂O₄ anode gathers electrons and engages with the Zn²⁺ in the electrolyte exclusively when charged. The formation of a dual electric layer occurs, with the CNTs cathode collecting positive ions and creating a similar electric double layer²⁻ in the electrolyte. Concurrently, the electrochemical properties of Ce, Co-ZnFe₂O₄, and the oxygen-rich groups in CNTs are capable of creating pseudocapacitance, resulting in the supercapacitor

exhibiting both double electric layer capacitance and pseudocapacitance. As depicted in the Fig. 31, during photoelectric collaborative charging, beyond the fundamental capacitance produced by charging, if the photon energy ($h\nu$) surpasses Ce Co-ZnFe₂O₄'s prohibited band width, light excites its valence band electrons, causing them to shift to the conduction band, before being conveyed to the current collector to add extra charge to the anode. Concurrently, stimulating the light will lead to the cathode gathering additional positive charges, consequently enhancing the supercapacitor's total capacitance. This further confirms the capability of the photoelectric cooperative charging mode to enhance the supercapacitor's specific capacity[56].

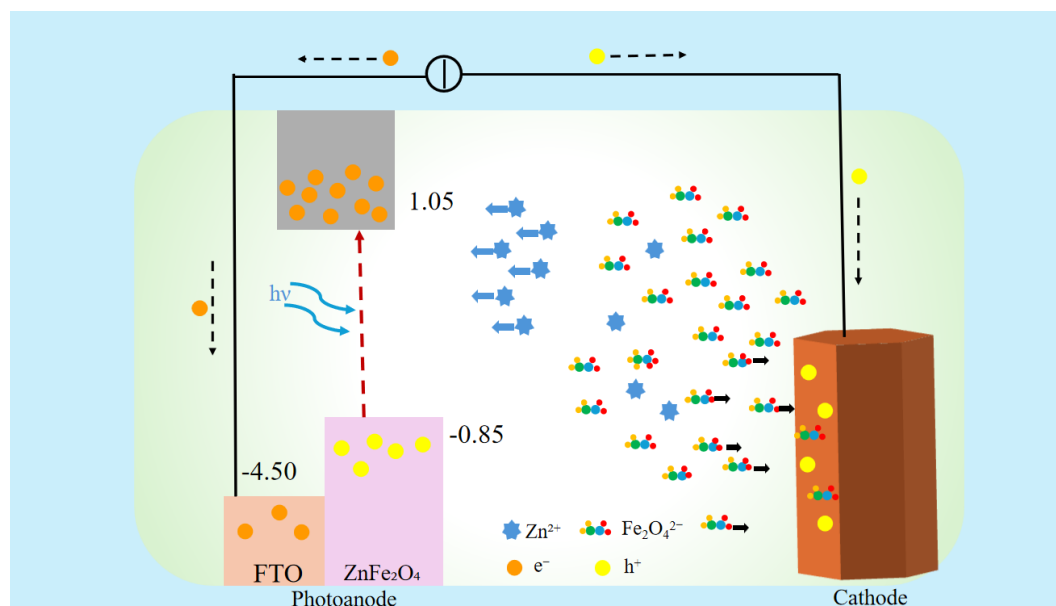


Fig. 31 Working principle diagram

As depicted in the Fig. 32 (ab), the GCD curve of the Ce,Co-ZnFe₂O₄ supercapacitor appears nearly triangular, indicating the supercapacitor's possession of both an electric double layer and pseudocapacitance attributes. Additionally, by keeping the current density the same, the supercapacitor achieves a significantly longer charging and discharging time in photoelectric cooperative charging mode compared to just depending on electric charging. Take, for instance, when the current density is 0.2 A/g, a supercapacitor's specific capacitance with electrical charging attains 292 F/g. Conversely, in photoelectric collaborative charging, this capacitance escalates to 313 F/g, marking a 7.2% rise in specific capacity. The outcome stems from the Ce,Co-ZnFe₂O₄ photoanode gathering light energy and transforming it into electrical power for storage. Regarding the particular role of the supercapacitor depicted in the Fig. 32 (c), maintaining identical charging scenarios, the supercapacitor's specific capacity diminishes as the current density rises[57-59]. For example,

with the exclusive use of charging, there's an increase in current density from 0.2 A/g to 0.5 A/g, and a decrease in specific capacitance from 132 F/g to 72 F/g. The cause lies in the increase in charge and discharge current density, resulting in electrolyte ions not having enough time to transition into the electrode material from the interface, thereby reducing the specific capacitance of the supercapacitor. Fig. 32 (d, e) displays the data on the retention rate and Coulomb efficiency of the Ce,Co-ZnFe₂O₄ supercapacitor. When the current density reaches 2A/g, the supercapacitor's Coulombic efficiency stabilizes at 100% following 10,000 instances of electrical charging, as shown in the Fig. 32 (d) or the illustration of photoelectric co-charging. Fig. 32 (e), showcasing its remarkable photoelectrochemical robustness. When charging, the retention rate of capacity attains 81%, while in the photoelectric collaborative charging setting, this proportion can soar to 90%. The information conclusively demonstrates the superior cycle stability of the supercapacitor we developed[60].

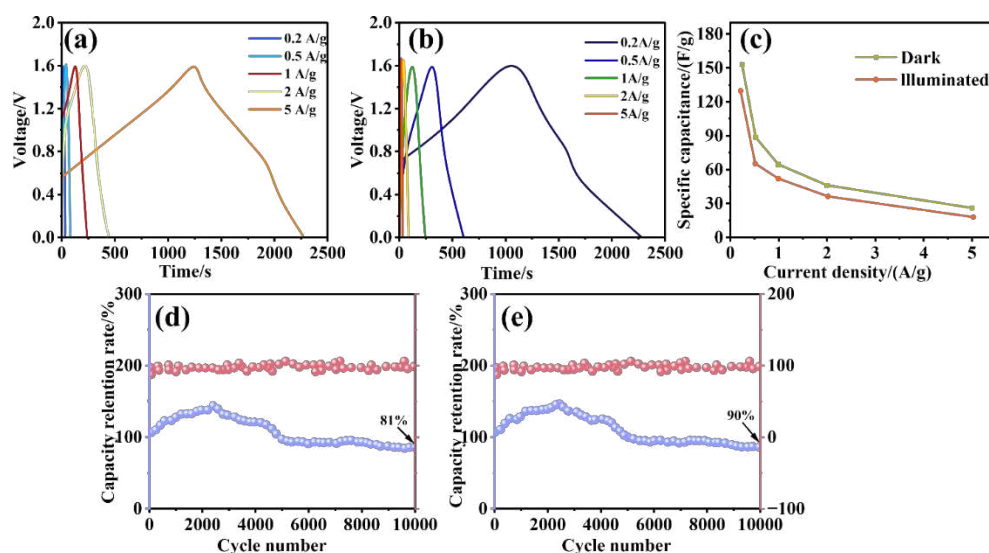


Fig. 32 (a, b) GCD curves, (c) specific capacity diagram, (e) Coulomb efficiency and capacity retention rate under (a, e) supercapacitor only electrical charging and (b) photoelectric synergistic charging conditions

Fig. 33 (a) depicts the changing trends in photovoltage and the effectiveness of photoelectric conversion (PCE) concerning the supercapacitor's charging time under circumstances where solely light is utilized for charging. During the initial phase of optical charging, the device's photovoltage escalates swiftly, hitting 0.58 V after 59 seconds of charging, equating to 68% of its peak voltage, and equates to a PCE of 0.29%, indicative of its superior rapid optical charging capability. With the gradual prolongation of the photocharging duration, the rate of photovoltage growth starts to decelerate. Following an hour of charging, the voltage peaked at 0.68 V[61,62]. Concurrently, the supercapacitor exhibited a specific capacitance of 74.63F/g, an energy density of 6.74Wh/kg, a power density of 35.61W/kg, and the PCE decreased to 0.05%. With the prolongation of charging duration, there will be a steady reduction in this PCE, primarily attributed to the heightened resistance of photoelectrons in transmitting to the current collector amid the rise in photovoltage[63]. Fig. 33 (b, c) displays the steady current charge and discharge (GCD) graphs for the supercapacitor, which is released in varying states following light charging. As depicted in the Fig. In item Fig. 33 (b), the supercapacitor first acquires a 0.6 V light charge, then emits it at different current densities in a light-free setting. In the initial phase of discharge,

the series resistance (R_s) of the device results in a decrease in voltage. Simultaneously, an increase in discharge current density leads to a steady decrease in discharge time and a parallel reduction in capacitance[64]. The reason behind this occurrence is that with rising charge and discharge rates, the $\text{Fe}^{2+}/\text{Fe}^{3+}$ and Zn^{2+} plasma within the electrolyte doesn't completely move inside the electrode, distancing it from the interface, leading to a reduction in specific capacitance. Fig. 33(c) illustrates that when the discharge current density remains constant, the duration of discharge under illuminated conditions exceeds that in the absence of light conditions. As an illustration, discharging at a rate of 0.1A/g results in a discharge duration of 531 seconds in illuminated environments, surpassing the 112-second period observed in no light scenarios. The reason lies in the fact that photocharging concurrently during the discharge phase prolongs the duration of the discharge. Fig. 33 (d) illustrates a unique experimental occurrence: the photovoltage attaining 0.3 V results in its discharge at a current density of 14mA/g. Stability in photovoltage is maintained even when it falls to 0.12V. Disabling the light source leads to a rapid decrease in voltage to 0 V, a phenomenon linked to the current density of discharge and photocharging being precisely identical at this juncture[65-66].

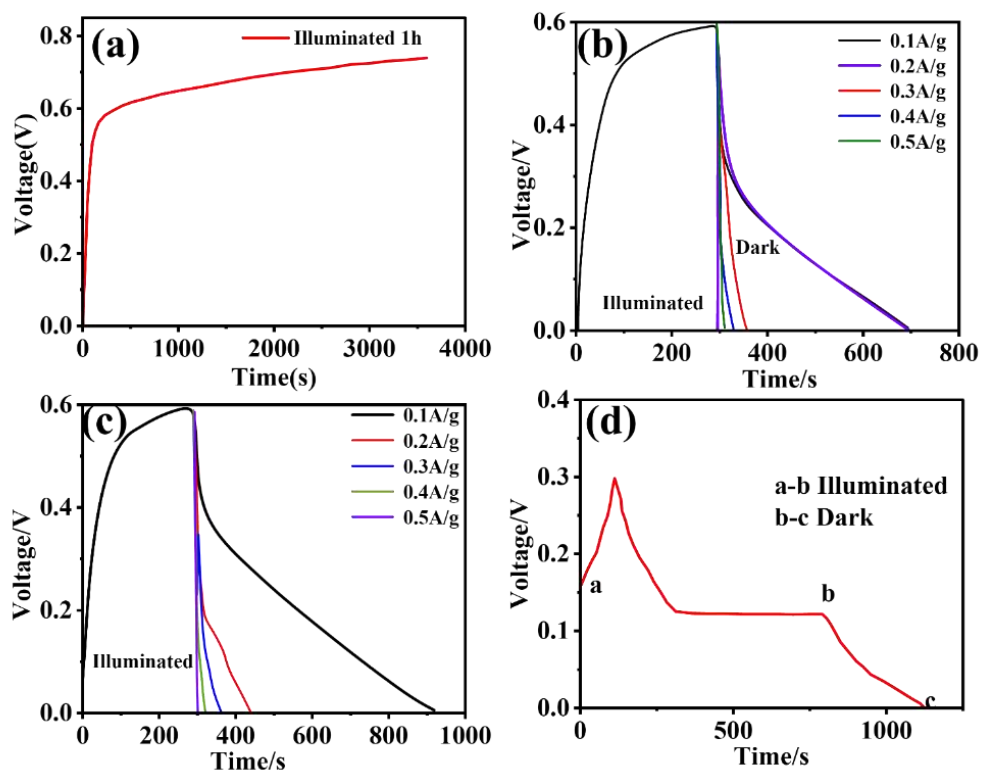


Fig. 33 The relationship between photocharging time and photovoltage of supercapacitors and the electrochemical properties of supercapacitors discharged under different conditions after photocharging

9 Conclusion

This study focuses on the energy and environmental issues caused by fossil fuel consumption. In view of the insufficient energy density of current supercapacitors, an in-depth study of high-energy supercapacitors composed of zinc ferrite cathode materials using Ce and Co as doping elements to induce oxygen vacancies and hydrophilic carbon nanotube anodes and its photoelectric properties was conducted. In this study, we first successfully prepared flower-like ZnFe_2O_4 . Subsequently, using microwave-assisted reaction and roasting technology, we obtained Ce-doped, Co-doped and Ce Co-doped ZnFe_2O_4 respectively. In addition, we have successfully produced hydrophilic carbon nanotubes by combining arc discharge technology and acidification modification methods. Through testing of physical properties and electrochemical properties, we found that 12 hours is the best reaction time and 0.5% is the best doping ratio. Under this condition, the Ce,Co co-doped ZnFe_2O_4 shows a specific surface area of $126.4 \text{ m}^2/\text{g}$ and stable electrochemical performance at various scanning rates. At 1 A/g , the electrode delivers a high specific capacity of 517 F/g with a capacity retention of 91.0%. The optimized Ce,Co- ZnFe_2O_4 cathode matching hydrophilic CNTs anode forms a stable asymmetric supercapacitor. After 10,000 cycles, the device retains 85% of its initial capacity, with an energy density of 12.5 Wh/kg . The photoelectric synergistic mode increases the specific capacity by 7.2% compared with traditional electric charging compared to the simple electric charging method, and performed better in terms of cycle stability. This research provides valuable reference for the development of high-performance supercapacitors. When compared with recently reported ZnFe_2O_4 -based electrodes modified by single doping or simple carbon hybridization, the Ce,Co co-doped $\text{ZnFe}_2\text{O}_4/\text{CNT}$ in this work exhibits more favorable charge transfer kinetics and structural stability. Moreover, the introduction of photoelectric synergy further boosts the capacitive performance, leading to a higher energy density among similar asymmetric supercapacitors. These results demonstrate the unique advantages and practical advancement of the present modification strategy. The enhanced cycling stability is further verified by EIS measurements before and after long-term cycling, which reveals the stable charge transfer and interfacial properties.

Author contributions

Pengxiang Ma: Supervision, data compilation. Changxu Qu: Investigation. Tingting Hao: supervision. Jian Hao: supervision. Yabin Wang: Conceptualization. Zheng Zhao: Investigation. Yongnan Tan: Data compilation. Kunxi Li: data compilation. Jingting Sun: formal analysis. Jing Wang: supervision, resources, funding acquisition.

Conflicts of interest

The authors declare no conflict of interest.

Data availability

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

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