Mesoporous Fe₃O₄@C nanoarrays as high-performance anode for rechargeable Ni/Fe battery

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ABSTRACT Rechargeable aqueous batteries with high power density and energy density are highly desired for electrochemical energy storage. Despite the recent reports of various cathode materials with ultrahigh pseudocapacitance exceeding 3000 F g⁻¹ (or 800 mA h g⁻¹), the development of anode materials is relatively insufficient, which limits the whole performance of the devices far from practical applications. Herein, we report the preparation of mesoporous Fe₃O₄@C nanoarrays as high-performance anode for rechargeable Ni/Fe battery by a self-generated sacrificial template method. ZnO/Fe₃O₄ composite was first synthesized by a co-deposition process, and ZnO was subsequently removed by alkali etching to construct the mesoporous structure. A thin carbon film was introduced onto the surface of the electrode by the carbonization of glucose to increase the structural stability of the electrode. The unique mesoporous nanoarray architecture endows the electrode with larger specific surface area, faster charge/mass transport and higher utilization of Fe₃O₄, which shows an ultrahigh specific capacity (292.4 mA h g⁻¹ at a current density of 5 mA cm⁻²) and superior stability in aqueous electrolyte (capacitance retention of 90.8% after 5000 cycles). After assembled with hierarchical mesoporous NiO nanoarray as a cathode, an optimized rechargeable Ni/Fe battery with double mesoporous nanoarray electrodes was fabricated, which provided high energy/power densities (213.3 W h kg⁻¹ at 0.658 kW kg⁻¹ and 20.7 kW kg⁻¹ at 113.9 W h kg⁻¹, based on the total mass of the active materials) in the potential window of 1.5 V with excellent cyclability (81.7% retention after 5000 charge/discharge cycles).

Keywords: Fe₃O₄, mesoporous, nanoarray, anode, Ni/Fe battery

INTRODUCTION

Energy storage in rechargeable batteries is paramount to our daily life; however, they are still far from perfect [1–3]. Lithium-ion batteries are widely regarded as the op-

timal power sources, but the risk of fire and explosion due to the use of flammable organic electrolytes greatly hinders their applications [4,5]. In contrast, aqueous rechargeable batteries featuring nonflammable water-based electrolytes are intrinsically safe, stable, and cost-effective [6,7]. Among various aqueous batteries, the alkaline Ni/Fe battery has attracted much attention because Ni and Fe are earth-abundant, ecofriendly, and rather cheap compared with other alternatives [8]. Despite these merits, the relatively low power/energy density and short cycle life of Ni/Fe battery limit their wide applications [9,10]. To improve their performance, delicate design and synthesis of nanostructured electrodes have been widely reported [11–16]. For example, hierarchical mesoporous NiO nanoarray with three-dimensional porous structure was fabricated, which delivered a super high specific capacitance (3114 F g⁻¹ at a current density of 5 mA cm⁻²) as a battery-type electrode [17].

Compared with the large capacitive and superior stable Ni-based cathode materials, Fe-based anode materials in Ni/Fe battery usually show poor stability, and the exploration of Fe-based anode electrodes is still unsatisfactory [18]. Iron owns multiple valence states and rich redox chemistry, enabling its high theoretical specific capacity within a wide potential range [19]. However, the multiphase transition of iron oxide can cause large volume expansion and pulverization of the active electrode film, resulting in a sharp decrease in capacity only within hundreds of cycles [20]. In order to reduce the loss of active materials during the electrochemical process, nanostructured electrodes were developed [21]. For example, a new type of ultrafast Ni/Fe battery was developed by using FeO_x nanoparticles/reduced graphene oxide sheets as an anode, which delivered the charge and discharge rates nearly 1,000 times that of conventional Ni/Fe batteries [22]. Conductive material coating (e.g.,

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carbon or conductive polymers) is also a solution to improve the structural stability of the electrodes [23,24]. For example, α -iron oxide nanorods were synthesized on the surface of highly conductive carbon nanotube fibers, and then coated with conductive polypyrrole to enhance electron, ion diffusion and cyclic stability [25]. However, how to prepare iron-based anode electrodes with both superior stability and high power/energy density is still a bottleneck of Ni/Fe batteries.

Herein, we deliberately developed mesoporous $\text{Fe}_3\text{O}_4@\text{C}$ nanoarrays ($\text{Fe}_3\text{O}_4@\text{C}$ MNAs) as high-performance anode material for rechargeable Ni/Fe batteries by a self-generated sacrificial template method. The mesoporous nanostructure was constructed by alkali etching of ZnO in prefabricated composites of ZnO/ Fe_3O_4 NAs, which provided the resulting Fe_3O_4 array with larger porosity and higher specific surface area. A thin film of carbon was coated on the surface of mesoporous Fe_3O_4 to increase the conductivity and structural stability. Consequently, the obtained $\text{Fe}_3\text{O}_4@\text{C}$ MNAs showed a specific capacity of $292.4 \text{ mA h g}^{-1}$ at a current density of 5 mA cm^{-2} , and a capacity retention rate of 90.8% at a current density of 30 mA cm^{-2} after 5000 cycles, outperforming most of the reported counterparts. Combining with hierarchical mesoporous NiO nanoarrays (NiO MNAs) as the cathode, a novel Ni/Fe battery system was fabricated, which exhibited a high energy density of $213.3 \text{ W h kg}^{-1}$ at a power density of 0.658 kW kg^{-1} and excellent electrochemical stability with a specific capacity retention rate of 81.7% after 5000 cycles.

EXPERIMENTAL SECTION

Synthesis of ZnO/ Fe_3O_4 NAs

All the reagents were of analytical grade and used as received without further purification. Zn/Fe hydroxide nanoarrays on carbon fiber paper were synthesized as precursor by a simple hydrothermal method. In a typical procedure, 2 mmol $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ with a molar ratio of 1:2 were mixed in 40 mL of distilled water at room temperature. And then, 8 mmol of NH_4F and 10 mmol of $\text{CO}(\text{NH}_2)_2$ were added into the mixture under vigorous stirring to form a clear solution. Carbon fiber paper (about $2 \text{ cm} \times 4 \text{ cm}$) was carefully cleaned with diluted HNO_3 solution in an ultrasound bath for 15 min, and then washed with acetone and absolute ethanol for 5 min in sequence under ultrasonic conditions. Finally, the carbon fiber paper was rinsed three times with distilled water. The aqueous solution and the carbon fiber paper were transferred into a 50-mL Teflon-

lined stainless steel autoclave, which was sealed, maintained at 373 K for 8 h, and then permitted to cool down to room temperature. The thin film on the carbon substrate was rinsed three times with distilled water and dried at 353 K for 2 h. Finally, the sample was put into a quartz tube and annealed at 673 K for 3 h under an argon atmosphere, and the ZnO/ Fe_3O_4 NAs were obtained. For comparison, ZnO/ Fe_3O_4 NAs with different molar ratios of Zn^{2+} to Fe^{2+} (1:1 and 1:4) were also prepared by a similar process.

Synthesis of Fe_3O_4 MNAs

Fe_3O_4 MNAs were prepared by immersing the ZnO/ Fe_3O_4 NAs in a 10 mol L^{-1} NaOH solution with vigorous agitation for 12 h to remove ZnO, and then the sample was rinsed three times with distilled water and dried at 353 K for 2 h.

Synthesis of $\text{Fe}_3\text{O}_4@\text{C}$ MNAs

The Fe_3O_4 MNAs were immersed in 0.1 mol L^{-1} glucose solution with vigorous agitation for 24 h, and then the samples were dried at 353 K for 2 h. Finally, the sample was put into a quartz tube and annealed at 873 K for 2 h under an argon atmosphere, and $\text{Fe}_3\text{O}_4@\text{C}$ MNAs were obtained. The loading of the $\text{Fe}_3\text{O}_4@\text{C}$ MNAs was confirmed by the mass difference of the carbon paper before and after synthesis, which was measured to be 1.8 mg cm^{-2} .

Material characterization

Powder X-ray diffraction (XRD) was performed on a Shimadzu XRD-6000 diffractometer with Cu $\text{K}\alpha$ radiation ($\lambda=1.54056 \text{ \AA}$) in the 2θ range from 25° to 70° . The morphology of the samples was characterized using a field-emission scanning electron microscope (SEM) (Zeiss SUPRA 55) operating at 20 keV. The structure and size of the products were characterized using a transmission electron microscopy (TEM) system (FEI Tecnai G² 20 S Twin). The structure and composition of the products were characterized using a high-resolution TEM (HRTEM) system (JEM 2100). Raman spectra were collected using a 514 nm laser with RM100 under ambient conditions, with a laser spot size of about $1 \mu\text{m}$. Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas.

Electrochemical measurements

Electrochemical measurements were carried out at 298 K in a standard three-electrode glass cell on a CHI 660D (Chenhua, Shanghai) workstation. The ZnO/ Fe_3O_4 NAs, Fe_3O_4 MNAs and $\text{Fe}_3\text{O}_4@\text{C}$ MNAs on the carbon fiber

paper (1 cm × 1 cm) were used as the working electrodes. A platinum electrode and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. A freshly prepared 2 mol L⁻¹ KOH aqueous solution was used as the electrolyte. The capacity (*C*) of a single electrode was calculated from the galvanostatic charge-discharge curves, by the equation:

$$C = i\Delta t/m\Delta V,$$

where *i* is the discharge current, Δt is the discharge time, *m* indicates the mass of the active material, and ΔV corresponds to the voltage window.

The Ni/Fe battery was fabricated with the Fe₃O₄@C MNAs as the negative electrode and hierarchical NiO MNAs as the positive electrode. Hierarchical NiO MNAs were prepared based on our previous work [17]. A hierarchical NiO MNAs electrode was combined with a Fe₃O₄@C MNAs negative electrode with 2 mol L⁻¹ KOH as the electrolyte to assemble the full cell. Energy density (*E*) and power density (*P*) of the Ni/Fe battery were calculated by the equations of $E = \frac{1}{m} \int_0^t iV(t)dt$ and $P = E/\Delta t$, where *i* is the discharge current; *t* is the discharge time; *m* indicates the mass of the active material, and *V* corresponds to the voltage change after a full charge or discharge process.

To obtain a stable Ni/Fe battery operated over a wide potential window, the mass ratio of negative electrode to positive electrode was decided according to the charge balance equations of $q_+ = q_-$, $q = mC\Delta V$ and $m_+/m_- = (C_-\Delta V_-)/(C_+\Delta V_+)$, where *q* is the charge, *m* is the mass, *C* is the specific capacitance obtained by the three-electrode testing, and ΔV is the voltage window of positive and

negative electrodes.

RESULTS AND DISCUSSION

The Fe₃O₄ MNAs were fabricated by a self-generated sacrificial template method (Fig. 1). Zn/Fe hydroxide NAs with diamond-shaped quadrangular prism morphology were first synthesized on the carbon fiber paper by hydrothermal co-deposition of Zn²⁺ and Fe²⁺ (Fig. S1a). Then, Zn/Fe hydroxide NAs were transformed into ZnO/Fe₃O₄ composite NAs by annealing under an argon atmosphere. After that, ZnO as the sacrificial template was removed from the composite by alkaline etching to construct mesoporous structure of Fe₃O₄ MNAs. Finally, the Fe₃O₄ MNAs were immersed into a glucose solution for 24 h, and then annealed at 873 K for 2 h under argon atmosphere to make a thin carbon coating on the surface of Fe₃O₄ MNAs to obtain Fe₃O₄@C MNAs. To optimize the mesoporous structure of the nanoarray, Zn/Fe hydroxide NAs with a varied molar ratio of Zn²⁺ to Fe²⁺ were first prepared. The morphology of the nanoarray is mainly dominated by zinc hydroxide with a diamond-shaped quadrangular prism when the molar ratio of Zn²⁺ and Fe²⁺ is larger than 1:2 (Fig. S1b) compared with a cylinder morphology determined by iron-based hydroxide when the molar ratio of Zn²⁺ to Fe²⁺ reduced to 1:4 (Fig. S1c). Theoretically, as the amount of Zn ions increases, the porosity of Fe₃O₄ MNAs will increase after etching. However, high Zn amount (Zn/Ni=1:1) resulted in the structure collapse after alkaline etching of ZnO template (Fig. S2). The morphology of the sample with a molar ratio of Zn²⁺ to Fe²⁺ of 1:2 did not show any significant change during the calcination and alkaline

Figure 1 Schematic illustration of the fabrication process of Fe₃O₄@C MNAs on carbon fiber paper.

etching processes, as indicated by the SEM shown in Fig. S3a and b, and this sample was selected as the optimal sample for subsequent processing to obtain $\text{Fe}_3\text{O}_4@\text{C}$ MNAs.

The morphology and structure of $\text{Fe}_3\text{O}_4@\text{C}$ MNAs were further investigated in details by SEM and TEM. As shown in the SEM images in Fig. 2a, the obtained $\text{Fe}_3\text{O}_4@\text{C}$ MNAs mostly preserve the morphology of their precursors, which are diamond-shaped quadrangular prisms with the average edge length of about 1 μm . The magnified SEM image of the inset of Fig. 2a reveals the rough surface of $\text{Fe}_3\text{O}_4@\text{C}$ MNAs, demonstrating the coverage of a thin layer of carbon. It can be seen from the TEM images in Fig. 2b that the nanoarrays are composed of many nanoparticles, and among them, numerous mesopores exist. HRTEM analysis performed on the $\text{Fe}_3\text{O}_4@\text{C}$ MNAs shows that a carbon layer uniformly covers the surface of each nanorod, and the thickness of the carbon layer is approximately 5–10 nm (Fig. 2c). A lattice space of 0.48 nm is observed, which relates to the (111) plane of cubic Fe_3O_4 . The selected area electron diffraction (SAED) pattern shows diffraction spots attributed to the (200), (331) and (511) planes (Fig. 2d), confirming the crystal structure of Fe_3O_4 .

The phase and composition of the product were verified by XRD. As shown in the XRD pattern of Zn/Fe

Figure 2 Typical SEM (a), TEM (b), HRTEM (c) images and SAED pattern (d) of $\text{Fe}_3\text{O}_4@\text{C}$ MNAs.

hydroxide NAs in Fig. S4a and $\text{ZnO}/\text{Fe}_3\text{O}_4$ NAs in Fig. 3a, all the strong peaks can be indexed into the cubic Fe_3O_4 (JCPDS No. 72-2303) and hexagonal ZnO (JCPDS No. 36-1451). While the diffraction peaks of ZnO are almost absent in the XRD patterns of Fe_3O_4 MNAs and $\text{Fe}_3\text{O}_4@\text{C}$

Figure 3 (a) XRD patterns (the peaks with mark of “#” correspond to the carbon fiber paper substrate); (b) EDX patterns; (c) Raman spectra; (d) N_2 adsorption-desorption isotherms of $\text{ZnO}/\text{Fe}_3\text{O}_4$ NAs, Fe_3O_4 MNAs and $\text{Fe}_3\text{O}_4@\text{C}$ MNAs.

MNAs, indicating that the ZnO matrix is removed during the etching process. The energy dispersive X-ray spectroscopy (EDX) spectra of the obtained samples are shown in Fig. 3b and Fig. S4b. Compared with the precursor ZnO/Fe₃O₄ NAs, the Zn peaks in the EDX spectrum of the Fe₃O₄ MNAs almost disappear, indicating most of ZnO are removed. Raman analysis was conducted to further investigate the carbon form in Fe₃O₄@C MNAs (Fig. 3c). Two distinguishable peaks at about 1355 and 1588 cm⁻¹ corresponding to D-band and G-band of carbon and two weak bands at 348 and 660 cm⁻¹ assigned to Fe₃O₄ were observed. The intensity ratio of I_D/I_G of Fe₃O₄@C MNAs is greater than that of Fe₃O₄ MNAs, confirming the existence of a porous carbon layer in Fe₃O₄@C MNAs [26]. The porosity and specific surface area of the samples were determined by the N₂-adsorption/desorption method. The typical IV isotherm with H3-type hysteresis loops ($P/P_0 > 0.4$) are observed in all the three samples of ZnO/Fe₃O₄ NAs, Fe₃O₄ MNAs and Fe₃O₄@C MNAs (Fig. 3d), indicating the presence of mesopores [27]. The specific surface area of Fe₃O₄ MNAs is 89.4 m² g⁻¹, much larger than that of ZnO/Fe₃O₄ NAs (45.8 m² g⁻¹), indicating that the porosity and specific surface area are greatly improved by constructing mesoporous structure. Meanwhile, the specific surface area of

Fe₃O₄@C MNAs further increases to 241.6 m² g⁻¹ because of the uniform coating of porous carbon film on the surface of the nanoarrays. The pore size distributions showed that the pore size of ZnO/Fe₃O₄ NAs is mainly 15–30 nm (Fig. S5). After etching, the total pore volume of Fe₃O₄ MNAs improved, and the mesopores of 10–20 nm increased significantly. Moreover, in the Fe₃O₄@C MNAs, the macropores above 50 nm increased with the mesopores as the dominant pore size. The structures with large surface area and porosity can fully increase the exposed active sites, improve the utilization efficiency of active ingredients and facilitate the electrolyte penetration into the electrode material, which are advantageous for improving the electrochemical properties of the electrode material.

The cyclic voltammogram (CV) and galvanostatic charge/discharge measurements were used to study the electrochemical performance of the samples in a 2 mol L⁻¹ KOH aqueous solution with a three-electrode cell. Fig. 4a shows typical CV curves of these samples in the potential range of -0.2 to -1.2 V (vs. SCE) at a scan rate of 5 mV s⁻¹. Carbon paper substrate shows negligible capacitance, except that, all the CV curves of the as-prepared nanoarray electrodes show a set of redox peaks at about -0.6 and -1.1 V, corresponding to the reversible

Figure 4 Electrochemical characterization of ZnO/Fe₃O₄ NAs, Fe₃O₄ MNAs and Fe₃O₄@C MNAs: (a) CV curves at 5 mV s⁻¹; (b) galvanostatic charge/discharge curves at 5 mA cm⁻²; (c) plots of specific capacity versus current density; (d) plots of average specific capacity versus cycle numbers of Fe₃O₄ MNAs and Fe₃O₄@C MNAs at a galvanostatic charge and discharge current density of 30 mA cm⁻².

Faraday transformation process between Fe(II) and Fe(III). Compared with ZnO/Fe₃O₄ NAs and Fe₃O₄ MNAs, the CV curve area of Fe₃O₄@C MNAs distinctly increases, illustrating the increase in capacity. Chronopotentiometry measurement further confirms this phenomenon. As shown in Fig. 4b, the discharge curves of samples have a significant deviation from the straight line, suggesting that the capacity mainly comes from the Faraday redox reaction. For Fe₃O₄@C MNAs, the specific capacity reached 292.4 mA h g⁻¹ (1051.9 F g⁻¹) at a current density of 5 mA cm⁻² (within a potential range of -0.2 to -1.2 V), which is higher than those of ZnO/Fe₃O₄ NAs (72.3 mA h g⁻¹, 260.0 F g⁻¹) and Fe₃O₄ MNAs (266.6 mA h g⁻¹, 959.3 F g⁻¹). In addition, capacity maintenance over a wide range of current densities is another important feature of practical applications. The CV curves of Fe₃O₄@C MNAs at different scan rates and galvanic charge and discharge time curves at different discharge currents are given in Fig. S6a and b. The CV curves show similar characteristics as the scan rates increase from 5 to 100 mV s⁻¹. Fig. 4c illustrates the relationship between specific capacity and current density of different samples. The specific capacitances of ZnO/Fe₃O₄ NAs, Fe₃O₄ MNAs and Fe₃O₄@C MNAs are 11.4, 57.4 and 122.2 mA h g⁻¹, respectively, when the current density increases from 5 to 50 mA cm⁻², showing the rate capability of 15.9%, 21.5% and 41.8% for each sample. It is worth noting that the specific capacitance and rate capability of Fe₃O₄@C MNAs are significantly higher than those of other samples, illustrating that suitable porosity is very important for high utilization of effective materials and mass transport during high-rate charging and discharging. Since the long-cycle performance is one of the most important performance indicators of the battery, the endurance test was conducted at 30 mA cm⁻² using galvanostatic charge-discharge cycles. Fig. 4d shows the specific capacity of Fe₃O₄ MNAs and Fe₃O₄@C MNAs as a function of cycle number for 5000 cycles. After 5000 cycles, the Fe₃O₄@C MNAs showed an overall decay of 9.2%, which is much lower than that of Fe₃O₄ MNAs (30.0% after 3000 cycles), confirming the superior structural stability due to the uniformly covered carbon film on the surface of the Fe₃O₄ MNAs.

As a further demonstration of advantages of the Fe₃O₄@C MNAs, a Ni/Fe battery was built by pairing the Fe₃O₄@C MNAs anode with hierarchical NiO MNAs cathode (Fig. 5a). Hierarchical NiO MNAs were prepared by the similar self-generated sacrificial template method [17] (Fig. 5b). To assemble the Ni/Fe battery, the mass ratio of the anode and cathode materials was balanced

based on the charge capacity, and the voltage window was set to be 1.5 V according to their individual potential window (Fig. S7). Fig. 5c shows the CV curves of the assembled Ni/Fe battery at different scan rates from 5 to 50 mV s⁻¹ at 0–1.5 V. Multiple sets of well-defined redox peaks appear, proving that their energy storage capacity mainly comes from Faradaic redox reactions. Even when the scan rate reaches 50 mV s⁻¹, well-defined redox pairs can be observed, which proves the fast charge and discharge performance of the battery and excellent capacitance performance. The performance of the Ni/Fe batteries was further evaluated by galvanostatic charge/discharge measurement at different current densities (0.5–10 A g⁻¹), as shown in Fig. 5d. Meanwhile, the obvious charging and discharging platforms in the curves prove that the battery-type reaction occurs during the energy storage process. To study the capacity reversibility of our Ni/Fe battery, the coulombic efficiencies at various current densities were calculated based on the galvanostatic charge/discharge curves, which is 81.0%, 92.4%, 94.7%, 97.7%, 99.8% and 99.8% for 0.5, 1, 3, 5, 8 and 10 A g⁻¹, respectively. The high coulombic efficiencies at higher current densities indicate that the capacity is reversible. However, at the low current density of 0.5 A g⁻¹, the coulombic efficiency is relatively low (81%), revealing that some side reactions, such as water splitting, may occur. This phenomenon is also confirmed by the asymmetric CV curves in Fig. 5c at low scan rate, which is commonly seen in aqueous batteries [28]. The specific capacity calculated by the discharge curves is 162.8 mA h g⁻¹ when the current density is 0.5 A g⁻¹. The Ragone plot in Fig. 5e illustrates the relationship between energy and power densities of the Ni/Fe battery. When the power density is 0.658 kW kg⁻¹, the energy density can reach 213.3 W h kg⁻¹. In addition, at a high power density of 20.7 kW kg⁻¹, the energy density can still reach 113.9 W h kg⁻¹. The energy density and power density of our as-fabricated battery are also impressive when compared with other reported aqueous Ni/Fe batteries, such as GF/CNTs/Ni(OH)₂//GF/CNTs/Fe₂O₃ (287 W kg⁻¹, 100.7 W h kg⁻¹) [12], FeS₂@carbon//NiO@carbon (1.43 kW kg⁻¹, 87.38 W h kg⁻¹) [18], Ni(OH)₂/MWNT//FeO_x graphene (1.6 W kg⁻¹, 141 W h kg⁻¹) [22], Ni//mc-FeO_x-C (0.7 kW kg⁻¹, 173.7 W h kg⁻¹) [29], Ni(OH)₂/NG//C-Fe nanoparticles (0.81 kW kg⁻¹, 101.0 W h kg⁻¹) [30], Ni-Co double hydroxide//Fe-550 (3.3 kW kg⁻¹, 82.3 W h kg⁻¹) [31], Ni₃S₂//Fe₂O₃-S@C (1.3 kW kg⁻¹, 45.64 W h kg⁻¹) [32] and Ni(OH)₂/NG//Fe (0.7 kW kg⁻¹, 136.7 W h kg⁻¹) [33]. More comparisons with the literatures are listed in Table S1. Furthermore, the hierarchical

Figure 5 Electrochemical performance of hierarchical NiO MNAs//Fe₃O₄@C MNAs Ni/Fe battery: (a) schematic representation of the fabricated Ni/Fe battery; (b) typical SEM image of the hierarchical NiO MNAs sample; (c) CV curves at scan rates of 5–50 mV s⁻¹; (d) galvanostatic charge/discharge curves at different current densities of 0.5–10 A g⁻¹; (e) Ragone plot related to energy and power densities of the Ni/Fe battery; (f) cycling performance at a constant current density of 10 A g⁻¹ and LED demo of the Ni/Fe battery device (inset).

NiO MNAs//Fe₃O₄@C MNAs battery also exhibits unexpectedly high stability, which is evaluated at a high current density of 10 A g⁻¹ (Fig. 5f). The hierarchical NiO MNAs//Fe₃O₄@C MNAs Ni/Fe battery displays excellent cycling stability with 81.7% retention of the initial specific capacity after 5000 cycles. In addition, a demonstration experiment with two tandem hierarchical NiO MNAs//Fe₃O₄@C MNAs Ni/Fe batteries lighting an LED light is also shown in Fig. 5f, which indicates the potential of hierarchical NiO MNAs//Fe₃O₄@C MNAs Ni/Fe battery in practical applications.

CONCLUSIONS

Mesoporous Fe₃O₄@C nanoarrays (Fe₃O₄@C MNAs)

were prepared by a self-generated sacrificial template strategy combined with a carbon coating method. Electrochemical tests show that the Fe₃O₄@C MNAs electrode exhibits excellent capacity performance (292.4 mA h g⁻¹, 1051.9 F g⁻¹), good rate capability and excellent long-term cycling performance. The improved energy storage performance can be ascribed to the high utilization efficiency of the active material and the fast electron transfer in the reaction process resulted from the large porosity and high specific surface area of the mesoporous structure. Moreover, a Ni/Fe battery made of hierarchical NiO MNAs and Fe₃O₄@C MNAs has been constructed, which shows high energy/power density (213.3 W h kg⁻¹ at a power density of 0.658 kW kg⁻¹ and 20.7 kW kg⁻¹ at an energy

density of 113.9 W h kg⁻¹) and outstanding cycle ability (~5000 times), indicating its potential as a candidate material for Ni/Fe battery.

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碳包覆介孔四氧化三铁纳米阵列：高性能Ni/Fe水相电池阴极材料

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摘要 阴极材料的开发对于可充电水相电池的发展具有重要意义. 本文通过自牺牲模板法和碳包覆法相结合制备了碳包覆介孔 Fe_3O_4 纳米阵列阴极材料($\text{Fe}_3\text{O}_4@\text{C}$ MNAs). 得益于包覆碳层、介孔结构和纳米阵列结构的优异特性, $\text{Fe}_3\text{O}_4@\text{C}$ MNAs电极表现出良好的倍率性能和优秀的循环稳定性. 在组装的Ni/Fe电池器件中, $\text{Fe}_3\text{O}_4@\text{C}$ MNAs表现出较高的能量密度及功率密度(在能量密度为 $213.3 \text{ W h kg}^{-1}$ 时功率密度为 0.658 kW kg^{-1} 和在功率密度为 20.7 kW kg^{-1} 时能量密度为 $113.9 \text{ W h kg}^{-1}$)和出色的循环稳定性(约5000次循环后保持81.7%).