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# Growth of 3D Nanoflower-Like FeCo<sub>2</sub>O<sub>4</sub>@Yb-Ni(OH)<sub>2</sub> Composites on Ni Foam As Advanced Electrodes for High-Performance Supercapacitors

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In this work, a 3D nanoflower-like Ni@FeCo<sub>2</sub>O<sub>4</sub>@Yb-Ni(OH)<sub>2</sub> composite was prepared via a facile liquid phase chemical deposition and electrochemical deposition method. The as-synthesized Ni@FeCo<sub>2</sub>O<sub>4</sub>@Yb-Ni(OH)<sub>2</sub> composites have a large specific surface area because of the developed nanoflower morphology, which creates good contact between the material and electrolyte. A high specific capacitance of  $11.04 \text{ F} \cdot \text{cm}^{-2}$  is reached at a current density of  $4 \text{ mA} \cdot \text{cm}^{-2}$ . More importantly, the asymmetric supercapacitor assembled by using the as-synthesized Ni@FeCo<sub>2</sub>O<sub>4</sub>@Yb-Ni(OH)<sub>2</sub> composites as the positive electrode and activated carbon as the negative electrode exhibits a high energy density of  $36.86 \text{ Wh} \cdot \text{kg}^{-1}$ , a power density of  $1.2 \text{ kW} \cdot \text{kg}^{-1}$  and excellent cycling stability (97.8% capacitance retention).

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As a novel type of energy storage device, supercapacitors have been significantly developed due to their high power density,<sup>1</sup> long cycle life,<sup>2-4</sup> wide range of operating temperatures,<sup>5</sup> and rapid charging.<sup>6</sup> The research on and application of this device primarily focus on energy storage for intermittent energy sources, such as portable electronic products,<sup>7</sup> hybrid electric vehicles,<sup>8</sup> and smart grids. Complex oxides<sup>9</sup> and hydroxides of transition metals<sup>10</sup> have been recently regarded as promising electrode materials for supercapacitors because of their excellent electrochemical performance, with a high reversible capacity,<sup>11</sup> structural stability,<sup>12</sup> and electrical conductivity.<sup>13,14</sup> Transition metal oxides are widely explored as active materials for supercapacitors due to their low cost, low toxicity, and high theoretical capacitance.<sup>15</sup> Some bimetallic oxides, such as  $MnCo_2O_4^{16}$  and  $NiCo_2O_4^{17-19}$  show excellent electrochemical performances in supercapacitors. Mixed FeCo<sub>2</sub>O<sub>4</sub> performs well due to its multiple oxidation states and high electrical conductivity. The complex oxides and hydroxides of transitional metals cannot be used as standalone units in supercapacitors, because the energy density of transitional metals is inferior to that of other materials.<sup>20,21</sup> Thus, developing novel materials for improving the specific capacitance at high operating voltage remains a challenge.<sup>2</sup>

Ni(OH)<sub>2</sub> has been widely applied as an electrode in capacitors because of its high specific capacitance.<sup>10,23</sup> Moreover, the costeffectiveness and availability of Ni(OH)2 in various morphologies further widen its application in electrochemistry.<sup>24,25</sup> In recent years, various morphologies of Ni(OH)<sub>2</sub> have been investigated to increase its specific surface area.<sup>26-28</sup> Among the two available crystalline types, the  $\alpha$ -Ni(OH)<sub>2</sub> types of structure comprises of stacked Ni(OH)<sub>2</sub> layers. Some anions can insert into the layers of  $\alpha$ -Ni(OH)<sub>2</sub> to balance the electric charge, which increases the discharge capacity.<sup>29</sup> The high capacitance of  $\alpha$ -Ni(OH)<sub>2</sub> is attributed to its exchange of more than one electron per Ni atom during charging and discharging. However, the drawbacks of the low electronic conductivity, poor stability in alkaline solutions, and inferior rate capability of  $\alpha$ -Ni(OH)<sub>2</sub> seriously limit its practical application.<sup>30</sup> Heteroelement metal ions are doped into  $\alpha$ -Ni(OH)<sub>2</sub> to enhance the intrinsic conductivity and improve the electrochemical performance of TMO/TMHO.<sup>31–33</sup> The conductivity of the  $\alpha$ -Ni(OH)<sub>2</sub> in supercapacitors can be improved by doping of  $Co^{2+.34}$  Dai et al.<sup>35</sup> reported the co-doping of Al and Co in NiAlCo-layered double hydroxide (LDH) nanoplates to enhance the stability of the LDH phase or  $\alpha$ -phase Ni(OH)<sub>2</sub>. Moreover,

improving ion adsorption and diffusion is an effective method to promote the rate performance of Ni(OH)<sub>2</sub>. Liu et al.<sup>36</sup> designed and prepared core–shell structure composites with  $\beta$ -Ni(OH)<sub>2</sub> and a Ni(BO<sub>2</sub>)<sub>2</sub> shell to enhance the ion adsorption of OH<sup>-</sup> in alkaline electrolytes. Doping with rare earth elements has recently received increasing interest for improving the electronic conductivity and increasing the charge transfer rate of metal oxides. Gao et al.<sup>37</sup> doped Y into  $\alpha$ -Ni(OH)<sub>2</sub> to achieve a high specific capacitance of 1860 F g<sup>-1</sup> in supercapacitors. Yb-doped  $\alpha$ -Ni(OH)<sub>2</sub> exhibits improved electrochemical properties due to the effect of Yb on  $\alpha$ -Ni(OH)<sub>2</sub>.<sup>38,39</sup>

In the current study, the 3D structure of  $FeCo_2O_4@Yb-Ni(OH)_2$  composites grown on Ni foam (NF) was synthesized through a facile liquid-phase chemical and electrochemical deposition method. Growing composite materials directly on NF can avoid a decrease in the content of active sites due to the use of binders.<sup>40</sup> Meanwhile, the unique 3D morphology of composites could provide a large specific surface area, which allows sufficient contact between the material and electrolyte.<sup>41</sup> The as-prepared 3D Ni@FeCo\_2O\_4@Yb-Ni(OH)\_2 composites exhibited a good electrochemical performance with a specific capacitance of 18.15 F cm<sup>-2</sup> at 4 mA cm<sup>-2</sup> within a voltage window of 0–0.52 V. Doping by Yb plays a key role in improving the cycling stability and specific capacitance of the electrode. On this basis, the Yb-doped composites can be a promising electrode materials for supercapacitors.

# Experimental

All chemical reagents were of analytical grade and were used without further purification. Iron (III) nitrate nonahydrate (Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O), cobalt (II) nitrate hexahydrate (Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O), nickel (II) chloride hexahydrate (NiCl<sub>2</sub>·6H<sub>2</sub>O), ethanol (C<sub>2</sub>H<sub>3</sub>OH) and oxalic acid (C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>) were purchased from Guoyao Chemical Co., Ltd. (Shanghai, China). Ytterbium (III) chloride hexahydrate (YbCl<sub>3</sub>·6H<sub>2</sub>O) was obtained from Macklin Biochemical Co., Ltd. All aqueous solutions were freshly prepared using high purity water (18 M $\Omega$  cm resistance).

**Pretreatment of Ni Foam.**—The NF substrate  $(2.5 \times 1.5 \text{ cm}^2)$  was ultrasonically cleaned with acetone, 1 M HCl, and deionized water for 10 min. Then, the cleaned NF was dried in a vacuum at 60 °C for 12 h.

Synthesis of  $FeCo_2O_4$  nanorods on NF.—The  $FeCo_2O_4$  nanorods were prepared according to the reported literature with little modification.<sup>42</sup> Typically, 0.581 g of  $Co(NO_3)_2 \cdot 6H_2O$ , 0.29 g of  $Fe(NO_3)_3 \cdot 9H_2O$  and 70 ml of deionized water were mixed and

stirred for 30 min. Then, the as-prepared NF, 20 ml of  $C_2H_5OH$  and the resulting solution were placed in a 250 ml three-necked flask. Once the temperature reached 80 °C, 50 ml of a  $C_2H_2O_4$  (1.58 g) solution was then slowly dropped into the three-necked flask. After being kept at 80 °C for 5 min, the stirring was stopped, and the mixture was then kept at 100 °C for 2 h. Finally, the sample was washed with deionized water several times and then dried under vacuum at 60 °C for 12 h. The dried sample was further annealed in air at 400 °C for 2 h under rate heating of 2 °C min<sup>-1</sup>.

Synthesis of Ni@FeCo<sub>2</sub>O<sub>4</sub>@Yb-Ni(OH)<sub>2</sub> composites.—Yb-Ni(OH)<sub>2</sub> was coated onto the surface Ni@FeCo<sub>2</sub>O<sub>4</sub> sample by a facile electrochemical deposition method. First, 1.6 g of NiCl<sub>2</sub>·6H<sub>2</sub>O and 0.002 g of YbCl<sub>3</sub>·6H<sub>2</sub>O were dissolved in 100 ml of deionized (DI) water to form the electrolyte solution. Electrochemical deposition was exploited by using a Ni@FeCo<sub>2</sub>O<sub>4</sub> as the working electrode, and a Hg/HgO electrode and Pt electrode were used as the reference electrode and counter electrode, respectively. The electrochemical deposition process was performed at a constant voltage at -1.0 V for 45 min. For comparison, the Ni@FeCo<sub>2</sub>O<sub>4</sub>@ $\alpha$ -Ni(OH)<sub>2</sub> was prepared in the absence of Yb by using the electrochemical deposition method and the I-t curve at the same conditions as described above.

Material characterization.- The structural characterization of the samples structures were carried outcharacterized on by X-ray diffraction (XRD) using a SmartLab Smartlab SE diffractometer (XRD) with Cu K<sub> $\alpha$ </sub> radiation (1 <sup>1</sup>/<sub>4</sub> 0.15406 Å). The XRD data were collected in the  $2\theta$  range from  $10^{\circ}$  to  $80^{\circ}$  and with the a scanning speed was of 10°/min. The size and morphology of the assynthesized samples were analyzed by field scanning electron microscopy (SEM, FEI Sirion 200 and JEOL JSM 6700 F) and transmission electron microscopy (TEM, JEOL-2010). Energy dispersive spectroscopy (EDS, Genesis Apollo X/XL) was used to determine the surface element distribution of composite materials. The surface chemical composition was studied by X-ray photoelectron spectroscopy using a Thermo ESCALAB 250Xi spectrometer with Al  $K_{\alpha}$  radiation The Raman spectra of the composites were measured by using a INVIA Raman microprobe (Renishaw Instruments, England). The infrared spectra of the samples were measured by a Nicolet FTIR spectrometer at room temperature in the range of  $3100 \sim 500 \text{ cm}^{-1}$ . The specific surface area and pore distribution of the electrode material were obtained by measuring N2 adsorption-desorption isotherms through the BrunauerEmmett-Teller (BET) and the Barrett-Joyner-Halenda (BJH) equations using a Tristar 3000 porosimeter. Thermal gravimetric differential thermal gravimetric analysis (TG-DTG) was performed for the Ni@FeCo<sub>2</sub>O<sub>4</sub>@Yb-Ni(OH)<sub>2</sub> composites by employing a thermogravimetric analyzer (TGA, TA Q500), under a flow of N<sub>2</sub> and with a heating rate of 10 °C min<sup>-1</sup>

*Electrochemical measurements.*—The electrochemical performance of the prepared electrode was evaluated using a threeelectrode configuration through an electrochemical workstation (CHI 660D) operated at room temperature. Cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) were used in this research. Ni@FeCo<sub>2</sub>O<sub>4</sub>@Ni(OH)<sub>2</sub> or Ni@FeCo<sub>2</sub>O<sub>4</sub>@Yb-Ni(OH)<sub>2</sub>, a platinum plate and a Hg/HgO electrode were utilized as the working electrode, counter electrode and reference electrodes, respectively. Then, the three-electrode system was immersed in a 6 M KOH electrolyte solution.

CV was conducted in a potential window of 0–0.55 V, and the GCD tests were performed in a potential range of 0–0.5 V. Electrochemical impedance spectroscopy (EIS) was performed in a frequency range from 100 kHz to 0.01 Hz by a scanning voltage of 5 mV. The area ratio capacitance of the samples was calculated by integrating of the CV curve according to the following equation:<sup>43</sup>

$$C_s = \frac{1}{UvS} \int I \, \mathrm{d}v \tag{1}$$

where  $C_s$  (F cm<sup>-2</sup>) is the area capacitance of the sample, U (V) is the voltage window, v (V s<sup>-1</sup>) is the scan rate, S (cm<sup>2</sup>) is the area of the working electrode, and  $\int I dv$  (A·V) is the voltammetric charge.

Another way to calculate the area ratio capacitance of the samples is by integrating of the discharge curve, as shown in the following formula:<sup>43</sup>

$$C_s = \frac{2i_s \int v dt}{\Delta v^2}$$
[2]

where  $C_s$  (F cm<sup>-2</sup>) is the area capacitance of the sample, t (s) is discharge time,  $\Delta v$  (V) is the voltage window, and  $i_s$  (A cm<sup>-2</sup>) is the current density of the constant discharge.

The specific volumetric capacitance ( $C_V$ , F cm<sup>-3</sup>) can be achieved using the following equation <sup>44</sup>:

$$C_V = C_s / h \tag{3}$$

where h is the total thickness of the electrode material.

The asymmetric supercapacitor device (ASC) was assembled by using the NF carrying active material as the positive electrode and active carbon (AC) as the negative electrode. Here, a cellulose paper substrate was pre-soaked in a 6 M KOH solution, and used as the separator membrane. The electrochemical performance of the ASC devices was determined on an electrochemical working station (CHI 660D).

The mass-specific capacitance can be evaluated using the following equation<sup>44</sup> in the two-electrode configuration.

$$C_m = \frac{2i_m \int v dt}{\Delta v^2}$$
[4]

where  $C_m$  is the mass-specific capacitance (F g<sup>-1</sup>),  $i_m$  is the current density (A g<sup>-1</sup>),  $\Delta v$  is the voltage window (V) and  $\int v dt$  is the galvanostatic discharge current area.

Oxalic acid was used as the complexing agent of metal salts in the synthesis of  $FeCo_2O_4$ . However, accurately measuring the amount of activated material in the positive electrode is difficult because of the strong corrosive effect of oxalic acid on Ni foam. Positive and negative charges are equal in supercapacitors (Eq. 5).

$$q_+ = q_-$$
 [5]

Thus, Eq. 6 is established.

$$I_{+}t_{+} = I_{-}t_{-}$$
 [6]

The mass of the negative electrode material was calculated by Eqs. 7-9

$$C_{-} = \frac{I_{-}t_{-}}{m_{-}v_{-}}$$
[7]

$$I_{+}t_{+} = C_{-}m_{-}v_{-}$$
[8]

$$m_{-} = \frac{I_{+}t_{+}}{c_{-}v_{-}}$$
[9]

where  $q_+$  and  $q_-$  are the charge amount for the positive and negative electrodes,  $I_+$  and  $I_-$  are the discharge current of the positive and negative electrodes,  $t_+$  and  $t_-$  are the discharge time of the positive electrode and negative electrodes, and  $m_+$  and  $m_-$  are the mass of active material in the positive electrode and negative electrode,



Scheme 1. Schematic diagram for the formation of  $FeCo_2O_4@Yb-Ni(OH)_2$  composite.

respectively. C- is the specific capacitance of the negative electrode.

Moreover, the energy density (E) and the power density (P) were calculated according to the following equations<sup>43</sup>:

$$E = \frac{I \int v dt}{M}$$
[10]

$$P = \frac{E}{t}$$
[11]

*E* is the energy density, I(A) is the current and M(g) is the total active mass of both electrodes.  $\int v dt$  is the galvanostatic discharge current area. *P* is the power density and *t* is the discharge time.

# **Results and Discussion**

Scheme 1 describes the process used to fabricate the  $FeCo_2O_4$ nanorod/Ni(OH)<sub>2</sub> composites on NF with two steps. First,  $Co(NO_3)_2 \cdot 6H_2O$  and  $Fe(NO_3)_3 \cdot 9H_2O$  were mixed with NF to synthesize the  $FeCo_2O_4$  nanorods on NF. A gray product was formed on the surface of NF by coprecipitating the mixture at 100 °C. After calcining of the product at 400 °C for 2 h, its color changed from gray to black, thereby indicating that  $FeCo_2O_4$ nanorods formed on the NF surface. Second,  $YbCl_3 \cdot 5H_2O$  and NiCl<sub>2</sub>·6H<sub>2</sub>O dissolved in water were used as an electrolytic solution, while the as-synthesized Ni@FeCo<sub>2</sub>O<sub>4</sub> was utilized as a working electrode in the three-electrode system. The Yb-doped  $\alpha$ -Ni(OH)<sub>2</sub> composites were successfully loaded onto the surface of Ni@FeCo<sub>2</sub>O<sub>4</sub> after electrochemical deposition. While preparing Yb-doped  $\alpha$ -Ni(OH)<sub>2</sub> by electrochemical deposition, a gas with a pungent odor could be observed. Furthermore, the wet potassium iodide-starch test paper near the counter electrode became blue, which indicated that Cl<sub>2</sub> formed in the counter electrode. The following reactions occurred during the electrochemical deposition process:

$$NiCl_2 + 2H_2O = Ni(OH)_2 + Cl_2 \uparrow + H_2 \uparrow$$

$$2YbCl_3 + 6H_2O = 2Yb(OH)_3 + 3Cl_2 \uparrow + 3H_2\uparrow$$

The SEM images of the Ni@FeCo<sub>2</sub>O<sub>4</sub> and Ni@FeCo<sub>2</sub>O<sub>4</sub> @Yb-Ni(OH)<sub>2</sub> composites are shown in Fig. 1. Figures 1a and 1b shows that the as-synthesized FeCo<sub>2</sub>O<sub>4</sub> on NF exhibits a uniform rod array morphology, while the average diameter of the rods is approximately 1  $\mu$ m. However, when Yb-doped  $\alpha$ -Ni(OH)<sub>2</sub> was modified onto the surface of the rod array, the formed nanoflower structure increased the specific surface area of the entire material, as presented in Figs. 1c and 1d. The space in the composites can be efficiently utilized due to the unique hierarchical structure, thereby facilitating the electrolyte ions to access the surface of the active materials. The TEM images (Figs. 1e and 1f) show the existing nanorod structure of FeCo<sub>2</sub>O<sub>4</sub> and the coated porous structure of the Yb-doped  $\alpha$ -Ni(OH)<sub>2</sub> composites on the nanorod surface. This result agrees well with the results of the SEM study.

The crystalline structure of the as-synthesized products was investigated by XRD analysis, as shown in Fig. 2. Line a shows the diffraction peaks at 31.3°, 36.9°, 44.8°, and 63.2°, which can be assigned to the (220), (311), (400), and (440) planes of the FeCo<sub>2</sub>O<sub>4</sub> spinel structure, respectively (PDF# 71–0816). Apart from these peaks, a series of weak peaks (2 $\theta$  values of 19.40°, 33.18°, 52.12°, and 59.1°) in line b can be indexed as the (001), (100), (102), and (110) planes, respectively, of hexagonal  $\alpha$ -Ni(OH)<sub>2</sub>(PDF# 38–0715). Regarding the hybrid composites of Ni@FeCo<sub>2</sub>O<sub>4</sub>@Yb-Ni(OH)<sub>2</sub> (line c), no evident signals attributed to Yb and Ni(OH)<sub>2</sub> could be observed, thereby implying the poor crystallinity of the Yb-doped Ni(OH)<sub>2</sub> obtained by electrochemical deposition at room temperature.<sup>45</sup> In addition to the typical diffraction peaks of hexagonal  $\alpha$ -Ni(OH)<sub>2</sub>, the characteristic peaks of Ni could be observed in line d, thereby indicating the formation of Ni@FeCo<sub>2</sub>O<sub>4</sub>@Ni(OH)<sub>2</sub>.



Figure 1. (a) Low- and (b) high-magnification SEM images of  $FeCo_2O_4$  onto the surface of Ni foam; (c) Low-and (d) high-magnification SEM images of  $Yb@Ni(OH)_2$  on  $FeCo_2O_4$ . TEM image of (e)  $FeCo_2O_4@Yb-Ni(OH)_2$  composites and (f)Yb-Ni(OH)\_2.



Figure 2. XRD patterns of (a) Ni@FeCo<sub>2</sub>O<sub>4</sub>, (b) FeCo<sub>2</sub>O<sub>4</sub>@ $\alpha$ -Ni(OH)<sub>2</sub> composites, (c) Ni@FeCo<sub>2</sub>O<sub>4</sub>@ $\gamma$ -Ni(OH)<sub>2</sub> composites and (d) Ni@FeCo<sub>2</sub>O<sub>4</sub>@ $\alpha$ -Ni(OH)<sub>2</sub> composites.

Furthermore, the surface elemental composition and chemical state in the as-synthesized composites was determined by XPS measurements, and the results are presented in Fig. 3. As shown in Fig. 3a, the survey spectrum reveals the existence of Fe, Co, Ni, O, Yb, and C in the composite. Figure 3b shows the high-resolution Fe2p spectra and the two main peaks at 711.5 and 724.3 eV, which correspond to Fe2p3/2 and Fe2p1/2, respectively. These peaks belong to Fe<sup>2+.46</sup> The fitting peaks (Fig. 3c) at 779.7 and 794.9 eV correspond to the Co2p3/2 and Co2p1/2 electron states in FeCo<sub>2</sub>O<sub>4</sub>. Furthermore, the ratio of areas of Co2p3/2:Co2p1/2 and Fe2p3/2:Fe2p1/2 are close to 2:1, the result is consistent with the reported reference.<sup>42</sup> Meanwhile, the weak peak at 786.6 eV indicates the satellite peak of  $Co^{3+.47}$  Figure 3d shows the two main peaks at 855.1 and 872.8 eV belonging to  $Ni2p_{3/2}$  and  $Ni2p_{1/2}$ , respectively, indicating the presence of Ni<sup>2+</sup> in the as-synthesized Ni@FeCo<sub>2</sub>O<sub>4</sub>@Yb-Ni(OH)<sub>2</sub> composite.<sup>48</sup> The Yb 4d spectrum is shown in Fig. 3e. As reported,<sup>49</sup> the Yb 4d spectrum is very complex, constructed of four or five peaks. Furthermore, Coulomb and exchange interaction can strongly affect the 4d spectrum of  $Yb^{3+}$ . The peak located at 188.8 eV is assigned to the 4d3/2. A dominant peak at 185.0 eV is ascribed to  ${}^{3}H_{6}$  and  ${}^{1}G_{4}$  terms, while a small peak at 192.5 eV is attributed to  ${}^{3}G_{6}$  and  ${}^{1}F_{3}$  terms. The peak at 199 eV is assigned to  ${}^{3}G_{4}$ .  ${}^{3}D_{3}$  and  ${}^{3}P_{2}$  terms. Figure 3f shows that

the O 1 s spectrum was divided into two fitting peaks, and the sharp peak at 531.6 eV is assigned to the existence of an H-O bond. The sharp peak at 531.6 eV indirectly proves the existence of Ni(OH)<sub>2</sub>. In addition, the fitting peak at 529.4 eV is caused by lattice oxygen. Thus, the as-synthesized composites were identified as Ni@FeCo<sub>2</sub>O<sub>4</sub>@Yb-Ni(OH)<sub>2</sub> composites.

SEM elemental mapping was conducted to study the distribution of elements in the Ni@FeCo<sub>2</sub>O<sub>4</sub>@Yb-Ni(OH)<sub>2</sub> composites, and the results are shown in Fig. 4. Figures 4a–4f shows the uniform distribution of Fe, Co, Ni, Yb, and O in the composites. The elemental content was evaluated accurately by performing energydispersive X-ray spectrometry microanalysis (Fig. 4g). The mass ratio of Fe, Co, Ni, Yb, and O is 1:2:16:1.5:16.5.

Moreover, the FTIR and Raman spectra were obtained to investigate the structure of the FeCo<sub>2</sub>O<sub>4</sub>@Yb-Ni(OH)<sub>2</sub> composites. As shown in Fig. 5a, the bands at 3428 and  $1637.9 \text{ cm}^{-1}$  can be assigned to the stretching and bending vibrations of absorbed water molecules, respectively. The weak peak at  $1380 \text{ cm}^{-1}$  can be attributed to the absorption peaks of the anions located between the Ni(OH)<sub>2</sub> layers. As a hexagonal system, Ni(OH)<sub>2</sub> is often regarded as a layered stack of NiO<sub>2</sub>. Due to the action of hydrogen bonds, some water molecules enter  $\alpha$ -Ni(OH)<sub>2</sub> layers and form  $[Ni(OH)_{2-x}(H_2O)_x]^{x+}$  with a positive charge. To maintain the electroneutrality, Cl<sup>-</sup> ions enter the  $\alpha$ -Ni(OH)<sub>2</sub> layers due to the NiCl<sub>2</sub> in the electrolyte, which is important in stabling the structure of  $\alpha$ -Ni(OH)<sub>2</sub>. The shift in the bending vibration of Ni–O–H from  $516 \text{ cm}^{-1}$  to  $659 \text{ cm}^{-1}$  is attributed to the effect of Yb. The FTIR spectra indicate the existence of many anions between the layers of Yb-doped Ni(OH)<sub>2</sub>, which can stabilize the composites. Figure 5b shows the Raman spectra of the FeCo<sub>2</sub>O<sub>4</sub>@Yb-Ni(OH)<sub>2</sub> composites. The signal at 305 cm<sup>-1</sup> is ascribed to an E-type vibration of Ni–OH, and the peak at 459 cm<sup>-1</sup> can be attributed to the stretching vibration of Ni–O in Ni(OH)<sub>2</sub>. The peak at  $522 \text{ cm}^{-1}$  may be related to the presence of defects in Yb-Ni(OH)<sub>2</sub>. The strong peak at  $1084 \text{ cm}^{-1}$  is mainly caused by the doped Yb in Ni(OH)<sub>2</sub>. The structural defects in Ni(OH)<sub>2</sub> doped with Yb facilitates the diffusion and transfer of Ni(OH)<sub>2</sub> protons. Thus, placing Yb-doped Ni(OH)<sub>2</sub> onto the FeCo<sub>2</sub>O<sub>4</sub> surface can result in the excellent electrochemical performance of the whole composites in a supercapacitor.

The  $N_2$  adsorption and desorption experiments were used to investigate the specific surface area and pore size distribution of the Ni@FeCo<sub>2</sub>O<sub>4</sub> and Ni@FeCo<sub>2</sub>O<sub>4</sub>@Yb-Ni(OH)<sub>2</sub> composites. A typical mesoporous type IV isotherm can be observed



Figure 3. XPS spectra of (a) survey scan, (b) Fe2p, (c) Co2p, (d) Ni2p, (e) Yb4d, (f) O1s of the Ni@FeCo2O4@Yb-Ni(OH)2 composite.



Figure 4. Mapping and EDS results of 3D FeCo<sub>2</sub>O<sub>4</sub>@Yb-Ni(OH)<sub>2</sub>.



Figure 5. FT-IR spectra (a) and Raman spectra (b) of FeCo<sub>2</sub>O<sub>4</sub>@Yb-Ni(OH)<sub>2</sub>.

in Fig. 6. Based on the isotherm curves of the FeCo<sub>2</sub>O<sub>4</sub> and FeCo<sub>2</sub>O<sub>4</sub>@Yb-Ni(OH)<sub>2</sub> composites, the specific surface areas are calculated as 14.7 and 21.1 m<sup>2</sup> g<sup>-1</sup>, respectively. This finding proves that loading Yb-Ni(OH)<sub>2</sub> on FeCo<sub>2</sub>O<sub>4</sub> increases the specific surface area of the whole material. The pore diameter distributions of FeCo<sub>2</sub>O<sub>4</sub> and FeCo<sub>2</sub>O<sub>4</sub>@Yb-Ni(OH)<sub>2</sub> are 9.57 and 9.54 nm, respectively (inset of Fig. 6). Hence, the contact area between the electrodes and electrolytes increases when the as-synthesized FeCo<sub>2</sub>O<sub>4</sub>@Yb-Ni(OH)<sub>2</sub> electrodes are applied in supercapacitors.

Figure 7 shows the TG-DTG plot of the FeCo<sub>2</sub>O<sub>4</sub>@Yb-Ni(OH)<sub>2</sub> composites obtained by scrapping off the NF. A weight loss event occurs below 100 °C (line a); thus, the crystalline water between the layers of Yb-Ni(OH)<sub>2</sub> and the adsorbed water molecules that weakly interact with the composite were gradually removed. The weight loss peak at 260 °C can also be atributed to the loss of hydration water in the composites and the thermal decomposition of Ni(OH)<sub>2</sub> into NiO. A mass loss of 5.5% can be calculated by following the TG curve (line b). FeCo<sub>2</sub>O<sub>4</sub> began to transform into Fe<sub>2</sub>O<sub>3</sub> and cobalt-rich



Figure 6. N<sub>2</sub> adsorption-desorption test and the pore diameter of Ni@FeCo<sub>2</sub>O<sub>4</sub> and Ni@FeCo<sub>2</sub>O<sub>4</sub>@Yb-Ni(OH)<sub>2</sub>.



Figure 7. The TG-DTG plot of FeCo<sub>2</sub>O<sub>4</sub>@Yb-Ni(OH)<sub>2</sub> composites.

spinel when the temperature reached 600 °C, thereby resulting in an approximately 2% mass loss of the composites. However, calculating the mass ratio of Yb is difficult due to its minimal doping in the composites. Similarly, the mass ratio of Fe and Co can't be obtained from the TG curve because of the complicated spinel structure of  $FeCo_2O_4$ .

Electrochemical performance of the as-synthesized composites in *a three-electrode system.*—The performance of the Ni@FeCo<sub>2</sub>O<sub>4</sub>@Yb-Ni(OH)<sub>2</sub> electrode, pure Ni@Yb-Ni(OH)<sub>2</sub>, Ni@FeCo2O4, and Ni@FeCo2O4@a-Ni(OH)2 composites was investigated by CV with a three-electrode system in a 6.0 M KOH aqueous electrolyte. Figure 8a shows the CV curves of Ni@Yb-Ni(OH)<sub>2</sub>, Ni@FeCo<sub>2</sub>O<sub>4</sub>, Ni@FeCo<sub>2</sub>O<sub>4</sub>@ $\alpha$ -Ni(OH)<sub>2</sub>, and Ni@FeCo2O4@Yb-Ni(OH)2 obtained with a scan rate of  $2 \text{ mV s}^{-1}$ . The result demonstrates that Ni@FeCo<sub>2</sub>O<sub>4</sub>@ $\alpha$ -Ni(OH)<sub>2</sub> and Ni@FeCo2O4@Yb-Ni(OH)2 have better electrochemical performances than pure Ni@FeCo<sub>2</sub>O<sub>4</sub> and Ni@Yb-Ni(OH)<sub>2</sub>. As shown in Fig. 8b, the Yb-doped Ni@FeCo2O4@Ni(OH)2 hybrid electrode presents a considerably longer discharging time than the Ni@FeCo<sub>2</sub>O<sub>4</sub>, Ni@ $\alpha$ -Ni(OH)<sub>2</sub> and Ni@FeCo<sub>2</sub>O<sub>4</sub>@Ni(OH)<sub>2</sub> electrodes at the same current density of  $4 \text{ mA cm}^{-2}$ . This result is consistent with the CV measurement. As shown in Figs. 8c and 8d, the maximum capacitance was achieved when the electrochemical deposition time was 45 min and the capacitance of sample-t45 was 7.1 F cm<sup>-2</sup> at a current density of 15 mÅ cm<sup>-2</sup> (sample-t30, samplet45, and sample-t60 represent electrochemical deposition times of 30, 45, and 60 min, respectively). The CV area and discharging time decrease when the electrochemical deposition time was over 45 min. Moreover, the Ni@FeCo<sub>2</sub>O<sub>4</sub>@Yb-Ni(OH)<sub>2</sub> composites prepared with different concentrations of the NiCl<sub>2</sub> electrolytic solution were explored, as shown in Figs. 8e and 8f. The results indicate

that the composites made with 15 mmol NiCl<sub>2</sub> had the best capacitance of  $8.63 \,\mathrm{F \, cm^{-2}}$  at a current density of 10 mA cm<sup>-2</sup>. Thus, 15 mmol of NiCl<sub>2</sub> and an electrochemical deposition time of 45 min were used to prepare the Ni@FeCo<sub>2</sub>O<sub>4</sub>@Yb-Ni(OH)<sub>2</sub> composites in the following experiments.

Figure 9a shows the CV curves of the Ni@FeCo<sub>2</sub>O<sub>4</sub> @Yb-Ni(OH)<sub>2</sub> composites, at obtained with different scan rates in a 6.0 M KOH aqueous solution. A clear redox peak located at 0.15 V was detected at the scan rate of 30 mV s<sup>-1</sup> and can be ascribed to Ni(OH)<sub>2</sub> oxidation in the composites. The excellent capacitance properties are related to the nanoflower morphology of the as-synthesized Ni@FeCo<sub>2</sub>O<sub>4</sub>@Yb-Ni(OH)<sub>2</sub> composites. Thus, the contribution of NF to the capacitance can be neglected. Due to the nanoflower structure of the as-synthesized Ni@FeCo<sub>2</sub>O<sub>4</sub> @Yb-Ni(OH)<sub>2</sub> composites, the electrolyte can maximize its contact time with the active material to shorten the migration distance of OH<sup>-</sup> and allow the electrochemical reaction to proceed rapidly. Thus, the surface redox reactions of the electrode proceeded according to the following Faradaic reactions. Figure 9b shows the GCD curves of the Ni@FeCo<sub>2</sub>O<sub>4</sub>@Yb-Ni(OH)<sub>2</sub> composites with a three-electrode system in a 6.0 M KOH aqueous electrolyte. The GCD curves obtained in a potential range of 0 to 0.52 V at different current densities demonstrated the proceeding Faradaic process. The calculated specific capacitances of the Ni@FeCo<sub>2</sub>O<sub>4</sub>@Yb-Ni(OH)<sub>2</sub> composites reached 11.04, 10.6, 9.44, 8.63, 7.02, and  $4.82 \text{ F cm}^{-2}$  at the current densities of 4, 6, 8, 10, 15, and 20 mA cm<sup>-2</sup>, respectively. At the same time, the  $C_V$  of the Ni@FeCo<sub>2</sub>O<sub>4</sub>@Yb-Ni(OH)<sub>2</sub> composites were 223.94, 215.01, 191.48, 175.05, 142.4 and  $97.77 \text{ F cm}^{-3}$  as the current density increases from 4 to  $20 \text{ mA cm}^{-2}$ . However, Fig. 9c shows the low specific capacitances of Ni@FeCo<sub>2</sub>O<sub>4</sub> under the same conditions, thereby indicating the important role of Yb-doped Ni(OH)<sub>2</sub> in the composites. As the current density increased, the specific capacity of the capacitor decreased due to the increased polarization of the Ni@FeCo<sub>2</sub>O<sub>4</sub>@Yb-Ni(OH)<sub>2</sub> electrode. The charge transfer on the electrode lags behind the voltage, thereby decreasing the capacitance at a high current density.

EIS tests were conducted to further evaluate the charge transfer and electrolyte diffusion occurring at the electrode/electrolyte interface of the as-synthesized composites.<sup>50</sup> Fig. 9d shows the corresponding Nyquist plots of the EIS spectra of the FeCo<sub>2</sub>O<sub>4</sub>, Ni@FeCo<sub>2</sub>O<sub>4</sub>, Ni@FeCo2O4@Ni(OH)2, and Ni@FeCo2O4@Yb-Ni(OH)2 electrodes, and the result was analyzed by an equivalent analog circuit. In the high-frequency region, the equivalent series resistance (Rs) of the electrochemical system was implied by the intersection on the real axis. The enlarged plots of the high-frequency region (Fig. 9d inset) demonstrate that the Rs values of FeCo2O4, Ni@FeCo2O4, Ni@FeCo<sub>2</sub>O<sub>4</sub>@Ni(OH)<sub>2</sub>, and Ni@FeCo<sub>2</sub>O<sub>4</sub>@Yb-Ni(OH)<sub>2</sub> are 0.47, 0.33, 0.42, and 0.36  $\Omega$ , respectively. Hence, FeCo<sub>2</sub>O<sub>4</sub> has a higher internal resistance than Ni@FeCo2O4. Moreover, the charge transfer resistance (Rct) values of  $Ni@FeCo_2O_4@Ni(OH)_2$  and Ni@FeCo<sub>2</sub>O<sub>4</sub>@Yb-Ni(OH)<sub>2</sub> are 0.21 and 0.18  $\Omega$ , respectively. Thus, Ni@FeCo2O4@Yb-Ni(OH)2 possesses a lower Rct than Ni@FeCo<sub>2</sub>O<sub>4</sub>@Ni(OH)<sub>2</sub>. Ion diffusion between the electrolyte solution and the surface of the electrode materials in the low-frequency region is shown in the line part. The approximate slope may explain Ni@FeCo2O4 and Ni@FeCo2O4@Yb-Ni(OH)2 having a better cycling stability than FeCo<sub>2</sub>O<sub>4</sub> and Ni@FeCo<sub>2</sub>O<sub>4</sub>@Ni(OH)<sub>2</sub>. The results further prove the excellent capacitance performance of the as-synthesized Ni@FeCo<sub>2</sub>O<sub>4</sub>@Yb-Ni(OH)<sub>2</sub>. Figure 9e shows the cycling performance of Ni@FeCo<sub>2</sub>O<sub>4</sub>@Ni(OH)<sub>2</sub> and Ni@FeCo<sub>2</sub>O<sub>4</sub>@Yb-Ni(OH)<sub>2</sub>, as obtained by the GCD tests performed with a current density of  $60 \text{ mA cm}^{-2}$  for 5000 cycles. Notably, the capacitance retention of the  $Ni@FeCo_2O_4@Ni(OH)_2$  electrode was only 64.6%. Moreover, the capacitance retention of the Ni@FeCo<sub>2</sub>O<sub>4</sub>@Yb-Ni(OH)<sub>2</sub> electrode was 80.9%. Furthermore, SEM was used to study the Ni@FeCo<sub>2</sub>O<sub>4</sub>@Ni(OH)<sub>2</sub> and



**Figure 8.** (a) Comparison of CV curves of typical Ni@Yb-Ni(OH)<sub>2</sub>, Ni@FeCo<sub>2</sub>O<sub>4</sub>, Ni@FeCo<sub>2</sub>O<sub>4</sub>@ $\alpha$ -Ni(OH)<sub>2</sub> and Ni@FeCo<sub>2</sub>O<sub>4</sub>@Yb-Ni(OH)<sub>2</sub> hybrid electrodes at scan rate of 2 mV s<sup>-1</sup>; (b) Comparison of GCD curves of Ni@Yb-Ni(OH)<sub>2</sub>, Ni@FeCo<sub>2</sub>O<sub>4</sub>@Yb-Ni(OH)<sub>2</sub> hybrid electrode; (c) CV curves and (d) GCD curves of the Ni@FeCo<sub>2</sub>O<sub>4</sub>@Yb-Ni(OH)<sub>2</sub> hybrid electrode with different electrochemical deposition time (sample-t30, 30 min; sample-t45, 45 min and sample-t60, 60 min); (e) CV curves and (f) GCD curves Ni@FeCo<sub>2</sub>O<sub>4</sub>@Yb-Ni(OH)<sub>2</sub> hybrid electrode in different concentrations of electrolyte (sample-C10, 10 mmol; sample-C15, 15 mmol and sample-C20, 20 mmol).



**Figure 9.** (a) CV curves of Ni@FeCo<sub>2</sub>O<sub>4</sub>@Yb-Ni(OH)<sub>2</sub> electrode at different sweep rates; (b) GCD curves of Ni@FeCo<sub>2</sub>O<sub>4</sub>@Yb-Ni(OH)<sub>2</sub> electrode at different current densities; (c) The corresponding graph of specific capacitance with current density and (d) EIS Nyquist plots, inset showing the enlarged picture of high-frequency region; (e) The cycling performance of Ni@FeCo<sub>2</sub>O<sub>4</sub>@Ni(OH)<sub>2</sub> and Ni@FeCo<sub>2</sub>O<sub>4</sub>@Yb-Ni(OH)<sub>2</sub> at the scan rate of 60 mA cm<sup>-2</sup>.

 $Ni@FeCo_2O_4@Yb-Ni(OH)_2$  composites after running for 4000 cycles in a supercapacitor to support the decreasing trend. As shown in Fig. 10a, the structure of  $Ni@FeCo_2O_4@Ni(OH)_2$  partly collapses after running for 4000 cycles. However, comparing with the morphology of  $Ni@FeCo_2O_4@Yb-Ni(OH)_2$  before (Figs. 1c–1d) and after running for 4000 cycles (Fig. 10b) indicates that the Ni@FeCo<sub>2</sub>O<sub>4</sub>@Yb-Ni(OH)<sub>2</sub> morphology minimally changes due to the maintained effect of Yb in  $\alpha$ -Ni(OH)<sub>2</sub>. Thus, the Yb doped in the composites plays a key role in improving the cycling stability and specific capacitance of the electrode.



Figure 10. The SEM of Ni@FeCo<sub>2</sub>O<sub>4</sub>@Ni(OH)<sub>2</sub> and Ni@FeCo<sub>2</sub>O<sub>4</sub>@Yb-Ni(OH)<sub>2</sub> after running 4000 cycle in a supercapacitor.

**Performance of Ni@FeCo\_2O\_4@Yb-Ni(OH)\_//AC asymmetric** capacitors.—The Ni@FeCo\_2O\_4@Yb-Ni(OH)\_2 electrode and AC were used as the positive and negative electrodes, respectively, to configure an asymmetrical supercapacitor in a two-electrode configuration (Ni@FeCo\_2O\_4@Yb-Ni(OH)\_2//AC ASC) with a 1 cm<sup>2</sup> area. This configuration was used to evaluate the possible application of the as-prepared composites in a supercapacitor. The electrochemical performance of the as-synthesized Ni@FeCo\_2O\_4@Yb-Ni(OH)\_2

composite was measured by CV, GCD, and cycle life analysis with different voltage ranges, scan rates, and current densities (Fig. 11). Figure 11a shows that the CV curves extended the potential windows to an operating range of 0 to 1.6 V at scan rates ranging from 10 mV s<sup>-1</sup> to 50 mV s<sup>-1</sup>. Figure 11b shows the GCD curves of the ASC at different current densities, which displays a high mass capacitance of  $115.2 \text{ F g}^{-1}$  at  $2 \text{ A g}^{-1}$ . Figure 11c shows that the capacitance retention of the as-fabricated Ni@FeCo<sub>2</sub>O<sub>4</sub>@Yb-Ni(OH)<sub>2</sub>//AC ASC was 98.2% after 5000 cycles were performed at a scan rate of  $100 \text{ mA cm}^{-2}$ . However, the capacitance retention of Ni@FeCo2O4@ Ni(OH)2//AC ASC was only 82.9% under the same conditions. The observed electrochemical stability of Ni@FeCo2O4@Yb-Ni(OH)2//AC ACS in a low current density of 40 mA cm<sup>-2</sup> was recorded for 5000 consecutive cycles (Fig. 11c) and confirmed only about 2.2% decrease from the initial capacitance retention. The result shows that the as-constructed Ni@FeCo<sub>2</sub>O<sub>4</sub>@Yb-Ni(OH)<sub>2</sub>//AC ACS has good cycle stability. The Ragone plots (Fig. 11d) show that the specific energy of the Ni@FeCo<sub>2</sub>O<sub>4</sub>@Yb-Ni(OH)<sub>2</sub> device can reach 36.86 Wh kg<sup>-1</sup> at a specific power of  $1200 \text{ W kg}^{-1}$ , which is much higher than



**Figure 11.** (a) CV curve and (b) GCD curves of  $FeCo_2O_4@Yb-Ni(OH)_2$  // AC asymmetric electrode; (c) Specific capacitance attenuation of the sample after charging and discharging for running 10000 cycles at 100 mA cm<sup>-2</sup>; (d) The ragone plots related to the power and energy densities of Ni@FeCo\_2O\_4@Yb-Ni(OH)\_2//AC and other asymmetric supercapacitors; (e) Two asymmetric capacitors are connected in series to light a red-light emitting diode (LED) (3.0 V); (f) Schematic diagram of asymmetric capacitor.

Fable I. '	The comp	parison of	power an	d energy	densities	of Ni@FeC	°02O4@Y	b-Ni(OH) <sub>2</sub> //A	C and	other a	asymmetric si	ipercaj	pacitors
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Sample	Energy density (Wh $kg^{-1}$ )	Power density (W kg <sup>-1</sup> )	References
FeCo <sub>2</sub> O <sub>4</sub> /MnO <sub>2</sub>	22.2	978	51
Ni(OH) <sub>2</sub> /NiS <sub>1.97</sub>	68.3	7662	29
MnCo <sub>2</sub> O <sub>4.5</sub> /Ni(OH) <sub>2</sub>	56.5	1900	52
FeCo <sub>2</sub> O <sub>4</sub> nanowire arrays	43	7200	53
Ni(OH) <sub>2</sub> /Fe <sub>2</sub> O <sub>3</sub>	45.4	6500	54
Ni(OH) <sub>2</sub> /Carbon Nanotube	50.6	95	55
Ni(OH) <sub>2</sub> /CNT	32.5	1800	55
NiO/rGO	32.5	375	56
Ni/MnO <sub>2</sub> /Ni(OH) <sub>2</sub>	9.4	4000	57
Ni@FeCo2O4@Yb-Ni(OH)2//AC	36.8	1200	This work

that of reported references, such as the values reported for  $FeCo_2O_4/MnO_2//AC$ ,  $MnCo_2O_{4.5}/Ni(OH)_2//AC$ , and  $Ni(OH)_2/$  CNT//AC (Table I). Figures 11e and 5f show a schematic of the asymmetric capacitor and images of a light-emitting diode (LED) (3.0 V, 20 mA) driven by two asymmetric capacitors in series. The capacitors can power the LED for 10 min after charging, thereby demonstrating the practical application of Ni@FeCo\_2O\_4@Yb-Ni(OH)\_2//AC ASC.

#### Conclusions

Overall, a simple liquid-phase chemical deposition method was used to prepare FeCo<sub>2</sub>O<sub>4</sub> nanorods on NF. To improve the specific capacitance and cycling stability of the active material, Yb-doped Ni(OH)<sub>2</sub> was coated onto the surface of Ni@FeCo<sub>2</sub>O<sub>4</sub> with the facile electrochemical deposition method. No complicated equipment or experimental conditions were used in the synthesis of to synthesize the Ni@FeCo<sub>2</sub>O<sub>4</sub>@Yb-Ni(OH)<sub>2</sub> composites. Yb plays an important role in improving the electrochemical performance of the whole composites. The as-synthesized Ni@FeCo<sub>2</sub>O<sub>4</sub>@Yb-Ni(OH)<sub>2</sub> delivered a high capacitance of 11.04 F cm<sup>-2</sup> at a scan rate of 4 mA cm<sup>-2</sup> and displayed a remarkable cycling stability, with a 97.8% capacitance retention after 5000 cycles were performed at a scan rate of 40 mA cm<sup>-2</sup>. The result demonstrates that the as-synthesized Ni@FeCo<sub>2</sub>O<sub>4</sub>@Yb-Ni(OH)<sub>2</sub> has potential for applications in energy storage and deserves further investigation.

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