Synthesis of graphene–NiFe$_2$O$_4$ nanocomposites and their electrochemical capacitive behavior

Zhuo Wang,$^a$ Xin Zhang,$^a$ Yang Li,$^a$ Zhaotie Liub and Zhengping Hao$^{a*}$

Reduced graphite oxide–NiFe$_2$O$_4$ (RGO–NiFe$_2$O$_4$) composites were synthesized by adding different amounts of NH$_3$·H$_2$O into a mixed aqueous solution of graphite oxide, Ni(NO$_3$)$_2$ and Fe(NO$_3$)$_3$ at room temperature. NH$_3$·H$_2$O was used to adjust the synthesis system's pH value. The morphology and the microstructure of the as-prepared composites were characterized by X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET) and transmission electron microscope (TEM) techniques. The structure characterizations indicate that NiFe$_2$O$_4$ successfully deposited on the surface of the RGO and the morphologies of RGO–NiFe$_2$O$_4$ show a transparent structure with NiFe$_2$O$_4$ homogeneously distributed on the RGO surfaces. Capacitive properties of the synthesized electrodes were studied using cyclic voltammetry and electrochemical impedance spectroscopy in a three-electrode experimental setup using 1 M Na$_2$SO$_4$ aqueous solution as electrolyte. It is found that the pH value plays an important role in controlling the electrochemical properties of these electrodes. Among the synthesized electrodes, RGO–NiFe$_{10}$ (pH = 10) shows the best capacitive properties because of its suitable particle size and good dispersion property. It could be anticipated that the synthesized electrodes will gain promising applications as novel electrode materials in supercapacitors and other devices by virtue of their outstanding characteristics of controllable capacitance and facile synthesis.

1 Introduction

Supercapacitors, have gained rapidly increasing attention because of their unique properties, such as high power density, long cycle life, and small size.1–5 Supercapacitors as energy storage devices can be used as a backup power source in portable electronic devices, pacemakers, hybrid electrical vehicles, and so on.4–6 They can be divided into two basic types according to their charge storage mechanism. One is electric double layer capacitance (EDLC), it generates capacitance from charge separation at the electrode–electrolyte interface;7,8 while the other is pseudocapacitance, it generates capacitance from fast Faradic reactions in the electrode material.9 Carbon materials are regarded as typical EDLC supercapacitors, where the capacitance depends on the specific area, pore structure and conductivity of the activate material. This kind of carbon material possesses a long cycle life and good mechanical properties. Metal oxides (MnO$_2$, Co$_3$O$_4$, RuO$_2$) and conducting polymers (polyaniline, polypyrrole and polythiophene)10–18 are typical pseudocapacitive materials that can achieve relatively high capacitance but are limited by poor cyclability due to structural degradation of the electrode through the redox process.19,20 So the capacitance can be enhanced by incorporating carbon materials with pseudocapacitive materials.

Owing to its various forms, carbon has gained extensive attention and wide use as a supercapacitor. Among the numerous carbon materials, graphene with its one-atom thick layer 2D structure, is newly found and has been widely investigated for its unique characteristics, such as chemical stability, high electrical conductivity, and large surface area.21 These encouraging characteristics provide such new materials with a wide range of potential applications and have attracted great interest in the development of graphene composites with other materials.17,22 However, the effective surface area of graphene materials depends highly on the layers, that is, single or few layers with agglomeration should be expected to exhibit a higher effective surface area. Therefore, numerous metal oxides and polymers have been added into graphene to enlarge the specific surface area of the pristine graphene. Recently, much work have been done on hybrid metal hydroxides or crystalline ferrites (such as NiAl-layered double hydroxide–graphene, CoAl-layered double hydroxide–graphene, MnFe$_2$O$_4$, CoFe$_2$O$_4$ and so on), because of their pseudocapacities.23–28 Besides, spinel transition metal oxides (AB$_2$O$_4$) with two metal elements provide the feasibility to tune the energy density and working voltage by varying the metal content.29,30 Among the AB$_2$O$_4$, it was reported that NiFe$_2$O$_4$ had been applied as anode material for LIBs with excellent electrochemical properties.21–31 Among
those reported, they mainly focused on techniques to prepare layered materials, these methods used are either time consuming and/or difficult for bulk-materials synthesis. Moreover, these studies did not address the effects of rigorous pH conditions on the supercapacitor performance. There are no systematic works on the pH effects on graphene–ferrite nanocomposite electrodes in supercapacitors compared with conventional metal oxide materials. Therefore, the development of a facile and large-scale synthesis is still in urgent need and valuable to be explored.

However, to the best of our knowledge, compared with other metal oxides, NiFe2O4 as a candidate pseudocapacitor has been less been studied, especially the electrochemical properties of NiFe2O4 combined with graphene. So graphene–NiFe2O4 nanocomposites could be synthesized to explore their potential as a supercapacitor. Importantly, they seldom focused on the influence of detailed conditions on the formation of the supercapacitor materials.

In the present work, graphene–NiFe2O4 nanocomposites are facilely synthesized and the influence of the pH value is discussed in detail. The electrochemical performances of the materials were investigated by cyclic voltammetry (CV), galvanostatic charge–discharge cycling and electrochemical impedance spectroscopy (EIS) studies, supercapacitor materials with high performances are expected to be synthesized and studied.

2 Experimental

2.1 Materials

Graphite (CP), Ni(NO3)2·6H2O (AR), Fe(NO3)3·9H2O (AR), HNO3 (AR) and H2SO4 were from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). NH3·H2O (AR) was purchased from Beijing Chemical factory (Beijing, China). All the materials were used as received without further purification.

2.2 Preparation of graphene oxide and graphene–NiFe2

(n = 8, 10, 12, 14) nanocomposites

Graphene oxide (GO) was prepared from natural graphite powder through a modified Hummers’ method.14 The hydrothermally reduced graphene was prepared by a modified method reported by Shi and co-workers.15 Graphene–NiFe2

(n = 8, 10, 12, 14) nanocomposites were prepared hydrothermally as follows, a certain amount of GO was dispersed in H2O and stirred for 12 hours to form a homogeneous aqueous dispersion. Then 0.3 g Ni(NO3)2 and 0.6 g Fe(NO3)3 were added into the GO dispersion followed by stirring at room temperature. NH3·H2O was added to the solution slowly and simultaneously to adjust the pH value to 8, 10, 12 and 14, respectively, then the mixture was transferred to a 100 mL Teflon-lined autoclave and maintained at 180 °C for 24 h for crystallizing. The products were washed with deionized water several times and dried at 50 °C for 24 h. The samples were denoted as RGO–NiFe2

(n = 8, 10, 12, 14) according to the different pH value. The formation of NiFe2O4 on the graphene surface can be represented as follows:16

\[
\text{NH}_3\cdot\text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OH}^- \\
\text{Fe}^{3+} + \text{OH}^- \rightarrow \text{Fe(OH)}_3 \\
\text{Fe(OH)}_3 \rightarrow \beta\text{-FeOOH} \\
\text{Ni}^{2+} + \text{OH}^- \rightarrow \text{Ni(OH)}_2 \\
\beta\text{-FeOOH} + \text{Ni(OH)}_2 \underset{\text{Hydrothermal}}{\rightarrow} \text{NiFe}_2\text{O}_4 + \text{H}_2\text{O}
\]

Apart from these reactions above, there was a side reaction:

\[
\beta\text{-FeOOH} \rightarrow \alpha\text{-Fe}_2\text{O}_3.
\]

2.3 Material characterization

Powder X-ray diffraction (XRD) patterns of all samples were carried out on a Rigaku powder diffractometer (D/MAX-RB) using Cu Kα radiation (λ = 0.15418 nm) at a scanning rate of 4° per min in 2θ = 10–70°. The structures of the electrode materials were characterized by transmission electron microscopy (TEM, JEOL 3010). Adsorption and desorption isotherms of nitrogen were measured with a NOVA 1200 gas sorption analyzer at liquid nitrogen temperature (−196 °C). Before the measurements, the samples were degassed under vacuum conditions at 120 °C for 8 h. The total pore volume was estimated from the amount of nitrogen adsorbed at a relative pressure of 0.99. The Brunauer–Emmett–Teller (BET) method was utilized to calculate the specific surface area using adsorption data acquired at a relative pressure (P/P0) range of 0.05–0.25. The pore size distribution curves were calculated from the analysis of the desorption branch of the isotherm based on the Barrett–Joyner–Halenda (BJH) algorithm. The micropore volume and micropore surface area were estimated by a t-plot method. Fourier transform infrared (FT-IR) spectroscopy was measured by the KBr method recorded on a Bruker Tensor 27, scanned from 4000 to 600 cm−1.

2.4 Electrochemical measurements

All the electrochemical measurements were carried out in a conventional three-electrode system in 1 M Na2SO4 aqueous electrolyte at room temperature. The as-synthesized electrode materials, a platinum wire electrode and a saturated calomel electrode (SCE) were used as working electrode, counter electrode and reference electrode, respectively. The working electrode was prepared by mixing the sample (80 wt%) as active material with poly(tetrafluoroethylene) (PTFE, 20 wt%) in ethanol to produce a homogeneous paste. Then the resulting mixture was coated onto the Ni foam substrate. The foam was dried at 80 °C in air for 12 h to remove the solvent. The electrochemical performance of the as-prepared material electrodes was tested using a cyclic voltammetry (CV) method, galvanostatic charge–discharge and electrochemical impedance spectroscopy (EIS) on an electrochemical workstation (CHI 660D, Shanghai CH Instrument Company, China). The measurements were carried out in 1 M Na2SO4 aqueous electrolyte at room temperature. CV tests were done between −1.2 V and −0.2 V (vs. SCE) at scan rates of 5, 10, 20, 30, 40, 50 and 100 mV s−1. Galvanostatic charge–discharge curves were measured in the potential range
of −1 to 0 V at different current densities, and the EIS measurements were carried out in the frequency range from 100 kHz to 0.1 Hz at open circuit potential with an ac perturbation of 5 mV.

3 Results and discussion

The formation of RGO–NiFe₂O₄ can be explained as follows (Scheme 1): metal cations were firstly adsorbed on the GO surface, using NH₃·H₂O as precipitation agent, then the reduction of GO and the crystallization of NiFe₂O₄ crystals happened in a one step process by the hydrothermal method. FT-IR spectra of graphene–NiFe₂O₄ composites, GO and RGO are shown in Fig. 1. The band around 3500 cm⁻¹ corresponds to the stretching vibration of absorbed water. The FT-IR spectrum of GO demonstrates the presence of C–O in carbonyl (νC=O at 1053 cm⁻¹), C–O in carboxylic acid (νC=O at 1243), and C=O in carboxylic acid and carbonyl moieties (νC=O at 1602 and 1731).

While for the spectrum of RGO, the characteristic peaks of C–O or C=O have disappeared, showing a good reduction. The peaks around 1400 cm⁻¹ exhibit the presence of O–H, which maybe because of the absorbed water. The wide broad band below 1000 cm⁻¹, is known as a common feature of all the ferrites.

To further investigate the formation of NiFe₂O₄, the power XRD patterns of graphene–NiFe₂O₄ nanocomposites are given in Fig. 2. The XRD spectra revealed that the graphene–NiFe₂O₄ nanocomposites prepared with different experimental conditions are similar and reveal the formation of cubic NiFe₂O₄ as compared with the standard pattern shown in Fig. 2. It can be observed that the intensity of XRD peaks decreased by increasing the pH value, which maybe because the NiFe₂O₄ amount on the RGO surface decreased.

The percentage of NiFe₂O₄ in the solid can be obtained from the comparison of the thermogravimetric profile of these nanocomposites (Fig. 3). The TGA curves of all the graphene–NiFe₂O₄ composites show a similar weight loss process,
however, the weight loss amount of them are quite different. These differences can be attributed to the different pH. The related data are given in Table 1. The amount of NiFe$_2$O$_4$ particles decreased with the raising of the pH value. This is in accordance with XRD results.

A TEM study gives the morphology of the RGO–NiFe$_2$O$_4$ nanocomposites from different experimental conditions (Fig. 4). These results show that the particles dispersed well on the surface of graphene with a transparent structure. Fig. 4 shows that the NiFe$_2$O$_4$ particles are uniformly distributed on the surface of RGO. The typical NiFe$_2$O$_4$ particle size is around 10 nm in diameter. However, it clearly shows that when the pH = 14, most of the particles are deposited together and more wrinkles in the graphene sheets were observed. It can be deduced that the pH played a critical role during the agglomeration of graphene sheets, this is in accordance with a previous report. So it is believed that the pH value has an important impact on the formation of NiFe$_2$O$_4$ particles. And the difference in the morphologies of NiFe$_2$O$_4$ synthesized under different conditions may influence the electrochemical capacitance properties as the EDLC contributed from the pore structure of a material.

As we know that the specific surface area of a material has an important impact on the capacitance of a material, the porous structure of the samples were characterised by nitrogen adsorption. These composites possess well-developed mesoporosity, reflected by their N$_2$ sorption isotherm and large N$_2$ uptake at low relative-pressure. However, the pore size distributions of them are not uniform and are different from each other (Fig. 5). As can be seen RGO–NiFe$_{10}$ possesses the widest range of pore size distribution. The surface areas and pore volume first increase and then decrease with rising pH value. A slight increase of the pH value results in a high surface area of 459.6 m$^2$ g$^{-1}$ and a pore volume of 0.395 cm$^3$ g$^{-1}$, both of which surpass those of the pristine graphene. Table 1 gives the BET data of these materials. The porosity initially increases with rising pH, but falls with a further increasing of pH value. Perhaps this is because a particular amount of metal nanoparticles is beneficial to the peeling of the graphene sheets, while further increasing the amount may lead to a stack of metal nanoparticles. Further, a sample with high specific surface area and mesopores is favorable for improving both the main pseudocapacitance of metals and the electric double-layer (EDL) capacitance of graphene because of the easily accessibility of the hydrated ions in the electrolyte to the exterior and interior pore surfaces.

The electrochemical behaviors of the obtained RGO–NiFe$_n$ nanocomposites have been investigated by CV, charge–discharge and EIS measurements. Fig. 6 shows CV curves of RGO–NiFe$_n$ ($n = 8, 10, 12, 14$), RGO and NiFe$_2$O$_4$ electrodes at a scan rate of 10 mV s$^{-1}$ in a 1 M Na$_2$SO$_4$ electrolyte between –1.2 and –0.2 V. Obviously, RGO–NiFe$_n$ composites show higher electrochemical activity than graphene and NiFe$_2$O$_4$. Besides the CV curves of RGO–NiFe$_{10}$ shows the highest integrated area of all the electrodes, which indicates excellent electrochemical performance of the electrode material. The good electrochemical performance of RGO–NiFe$_{10}$ can be ascribed to the appropriate experimental conditions leading to less aggregation of graphene sheets and good dispersion of NiFe$_2$O$_4$ nanoparticles on the surface of graphene, thus leading to a higher active surface area for charge storage as reported. Fig. 6b shows the CV curves of RGO–NiFe$_{10}$ at different scan rates (5, 10, 30, 50, 100 mV s$^{-1}$). It can be seen that with the increase of the sweep rate, a clear deviation from the rectangular shape was observed, which mainly resulted from the low interaction between the Na$^+$ and the electrode. The specific capacitances ($C_s$) were calculated from the CV curves according to the following equation:

$$C_s = \frac{\int I dV}{\text{mass} \Delta V}$$

where $C_s$ is the specific capacitance based on the mass of electroactive materials (F g$^{-1}$), $I$ is the response current (A), $\Delta V$
is the potential window (V), \( v \) is the potential scan rate (mV s\(^{-1}\)), and \( m \) is the mass of the electroactive materials in the electrodes (g). The specific capacitance values calculated from the CV curves of RGO–NiFe\(_8\), RGO–NiFe\(_{10}\), RGO–NiFe\(_{12}\) and RGO–NiFe\(_{14}\) at 5 mV s\(^{-1}\) are 153.13, 218.47, 150.45 and 112.88 F g\(^{-1}\), respectively. Table 2 gives the specific capacitance data of these electrodes. These values are larger than those reported for NiFe\(_2\)O\(_4\), showing an enhanced capacitance behavior by introducing graphene.

In order to further investigate the performance of electrode materials, galvanostatic charge–discharge tests of RGO–NiFe\(_n\) \((n = 8, 10, 12, 14)\) were conducted in 1 M Na\(_2\)SO\(_4\) with different current densities in a voltage range of \(-1\) to \(0\) V, as shown in Fig. 7. The specific capacitances \((C_s)\) of the electrodes can be calculated according to the following equation:

\[
C_s = \frac{It}{(\Delta V)m}
\]

where \( m \) (g) is the mass of the active material in the film electrode, \( I \) (A) is the discharge current, \( \Delta V \) (V) is the potential window, \( t \) is the discharge time, and \( C_s \) (F g\(^{-1}\)) is the specific capacitance. Table 3 lists the charge–discharge data of the electrode materials calculated from the above equation at different current density. The remarkably increased capacitance of RGO–NiFe\(_{10}\) is in accord with the trend of the \( C_s \) calculated from the CV curves. The reason for the increased capacitance of

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**Table 2** Specific capacitance values of electrodes calculated from cyclic voltammetry curves measured at different scan rates

<table>
<thead>
<tr>
<th>Sample</th>
<th>5 mV</th>
<th>10 mV</th>
<th>20 mV</th>
<th>30 mV</th>
<th>40 mV</th>
<th>50 mV</th>
<th>100 mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>RGO–NiFe(_8)</td>
<td>153.13</td>
<td>130.21</td>
<td>115.10</td>
<td>107.99</td>
<td>103.52</td>
<td>100.42</td>
<td>86.72</td>
</tr>
<tr>
<td>RGO–NiFe(_{10})</td>
<td>218.47</td>
<td>152.50</td>
<td>119.37</td>
<td>106.25</td>
<td>98.44</td>
<td>92.26</td>
<td>79.99</td>
</tr>
<tr>
<td>RGO–NiFe(_{12})</td>
<td>150.45</td>
<td>108.04</td>
<td>84.38</td>
<td>74.40</td>
<td>69.42</td>
<td>65.54</td>
<td>55.18</td>
</tr>
<tr>
<td>RGO–NiFe(_{14})</td>
<td>112.88</td>
<td>94.32</td>
<td>84.09</td>
<td>79.10</td>
<td>78.22</td>
<td>76.29</td>
<td>64.13</td>
</tr>
<tr>
<td>RGO</td>
<td>93.50</td>
<td>83.21</td>
<td>71.88</td>
<td>64.50</td>
<td>58.13</td>
<td>52.13</td>
<td>33.28</td>
</tr>
</tbody>
</table>
RGO–NiFe_{10} is discussed above. Besides, all the values calculated by the galvanostatic charge–discharge tests are higher than the previously reported RGO synthesized by us.\(^4\) The increase may be caused by the combination of electric double-layer capacitance of RGO and the peeling of graphene sheets with the addition NiFe_{2O4} nanoparticles. With increasing current density, the capacitance of the electrode is decreased from 345 F g\(^{-1}\) to 101.8 F g\(^{-1}\). The decreasing trend of the capacitance indicates that the partial surface of the electrode is inaccessible at a high current density. However, it is apparent that the shapes of the discharge curves of the RGO–NiFe\(_n\) deviate from the ideal voltage–time curves.\(^4\)\(^5\)\(^6\)\(^7\) The Nyquist plots generated from the impedance data for the composites are shown in Fig. 7b. Comparing the impedance plots of these electrodes, it is apparent that the values of \(R_s\) gradually increase with raising pH value. The almost vertical shape, representing the swelling diffusion in electrolyte and the adsorption onto the electrode surface, suggests the ideal capacitive behavior of the RGO–NiFe\(_n\). In addition, the long-term stability is considered in the selection of electrode materials in supercapacitor applications. The electrochemical stability of the RGO–NiFe_{10} electrode is examined by charge–discharge cycling at a constant current density of 10 A g\(^{-1}\). As shown in Fig. 8, the capacitance increased, which could be because the active material was not fully used. Then the capacitance decreased, and maintained stability after the 300\(^{th}\) cycle.

<table>
<thead>
<tr>
<th>Sample</th>
<th>1 A g(^{-1})</th>
<th>2 A g(^{-1})</th>
<th>3 A g(^{-1})</th>
<th>4 A g(^{-1})</th>
<th>5 A g(^{-1})</th>
</tr>
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<tbody>
<tr>
<td>RGO–NiFe(_8)</td>
<td>239.7</td>
<td>136.3</td>
<td>104.3</td>
<td>100.3</td>
<td>48.2</td>
</tr>
<tr>
<td>RGO–NiFe(_{10})</td>
<td>345.0</td>
<td>252.3</td>
<td>161.8</td>
<td>152.4</td>
<td>101.8</td>
</tr>
<tr>
<td>RGO–NiFe(_{12})</td>
<td>181.9</td>
<td>154.4</td>
<td>69.8</td>
<td>57.8</td>
<td>48.3</td>
</tr>
<tr>
<td>RGO–NiFe(_{14})</td>
<td>118.1</td>
<td>109.5</td>
<td>81.0</td>
<td>57.2</td>
<td>51.4</td>
</tr>
</tbody>
</table>

RGO–NiFe\(_{10}\) is discussed above. Besides, all the values calculated by the galvanostatic charge–discharge tests are higher than the previously reported RGO synthesized by us.\(^4\) The increase may be caused by the combination of electric double-layer capacitance of RGO and the peeling of graphene sheets with the addition NiFe_{2O4} nanoparticles. With increasing current density, the capacitance of the electrode is decreased from 345 F g\(^{-1}\) to 101.8 F g\(^{-1}\). The decreasing trend of the capacitance indicates that the partial surface of the electrode is inaccessible at a high current density. However, it is apparent that the shapes of the discharge curves of the RGO–NiFe\(_n\) deviate from the ideal voltage–time curves. After the \(iR\) drop, with the decrease of the voltage, the increase of the time deviates from a straight line. A similar phenomenon has already been reported by Xu et al., Niu et al. and Beidaghi et al. for electrochemically modified graphite electrodes, porous C-cloth material and electrochemically activated carbon micro-electrode arrays, respectively.\(^\text{41-43}\) The factors contributing to the non-ideal behavior can be illustrated as follows: (i) the pseudocapacitance from metal oxides; (ii) the redistribution of charge within the pores of the activated electrodes during charging or discharging; (iii) the effect of direct equivalent series resistance (ESR).

ESR is an important parameter determining the fundamental behavior of electrode materials for supercapacitors. Supercapacitors generally behave as pure resistors at high frequencies and typical capacitors at low frequencies. In the high frequency region, a semicircle due to charge transfer resistance on the electrode–electrolyte interface is observed. The region between the high frequency and low frequency is called the Warburg region and this is a combination of both resistive and capacitive behavior characterized by diffusive resistance. The low frequency region is mainly characterized by purely capacitive behavior. The intersection of the semicircle on the real axis at high-frequency represents the equivalent series resistance (\(R_s\)) of the electrode, while the diameter of the semicircle corresponds to the charge-transfer resistance (\(R_{ct}\)) of the electrodes and electrolyte interface.\(^\text{44}\) The Nyquist plots generated from the impedance data for the composites are shown in Fig. 7b. Comparing the impedance plots of these electrodes, it is apparent that the values of \(R_s\) gradually increase with raising pH value. The almost vertical shape, representing the swelling diffusion in electrolyte and the adsorption onto the electrode surface, suggests the ideal capacitive behavior of the RGO–NiFe\(_{10}\). In addition, the long-term stability is considered in the selection of electrode materials in supercapacitor applications. The electrochemical stability of the RGO–NiFe_{10} electrode is examined by charge–discharge cycling at a constant current density of 10 A g\(^{-1}\). As shown in Fig. 8, the capacitance increased, which could be because the active material was not fully used. Then the capacitance decreased, and maintained stability after the 300\(^{th}\) cycle.
4 Conclusions

In conclusion, we realized a facile synthesis of RGO–NiFe$_n$ composites by a hydrothermal process, and investigated the impact of the pH value in the synthesis process of supercapacitor materials. Additionally, it is believed that a controllable capacitance can be obtained by adjusting the pH value. Their electrochemical properties as supercapacitors were discussed in detail: it is found that well dispersed and suitable particle size leads to good electrochemical properties. The resulting composites exploit the benefits of the pseudocapacitive nature of the metal oxide and conductive EDLC nature of the RGO, implying a good application potential for supercapacitors as well as other power source systems.

Acknowledgements

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