Facile fabrication of mesoporous N-doped Fe₃O₄@C nanospheres as superior anodes for Li-ion batteries

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Experimental section

Fabrication of mesoporous N-doped Fe₃O₄@C nanospheres

First, 0.40 g arabic gum (AG), 0.65 g FeCl₃·6H₂O, 0.59 g Na₃Cit·2H₂O, and 1.20 g urea are successively dissolved in 25 mL ethylene glycol (EG) by sonication. Then, the as-prepared solution was transferred into a 50 mL Teflon-lined stainless steel autoclave and solvothermally treated in an air-flow electric oven at 200 °C for 10 hours. After cooling to room temperature, the AG coated magnetic (denoted as Fe₃O₄@AG) nanoparticles were collected by a magnetic bar, washed with ethanol and dried at 60 °C. Finally, the Fe₃O₄@AG nanoparticles were annealed at 450 °C for 4h under the N₂ atmosphere to give the mesoporous N-doped Fe₃O₄@C (denoted as N-mFe₃O₄@C) nanospheres.

For comparison, the citrate stabilized Fe₃O₄ nanoparticles (denoted as Cit-Fe₃O₄) were also synthesized without adding AG and carbonized (denoted as Cit-Fe₃O₄@C) in the same way.

Characterization

Transmission electron microscopy (TEM) images were obtained on a Hitachi H-800 electron microscope at an acceleration voltage of 200 kV with a CCD camera. Thermogravimetric (TGA) curves were obtained on a STA 449 C Jupiter (NETZSCH) thermogravimetry analyzer. X-Ray diffraction (XRD) analysis was performed on an X-ray diffractometer, Model Rigaku Ru-200b, using a nickel-filtered Cu Kα radiation. X-ray photoelectron spectroscopic (XPS) analysis was done on an ESCALAB 250 spectrometer. Raman spectrum was recorded using a Horiba Jobin-Yvon micro Raman spectrometer, equipped with a microscope and a laser of 633 nm as the excitation source. N₂ adsorption-desorption measurements were conducted on a Micromeritics ASAP 2010 instrument. The pore size distribution was calculated from the desorption branch of the isotherm by the Barrett-Joyner-Halenda (BJH) method. The specific surface area was calculated by using BJH and Brunauer-Emmett-Teller (BET) method. The elemental analysis was performed on a Vario Micro Elementar.

Electrochemical measurements

Electrodes were prepared by coating a copper foil substrate with the slurry of the active materials (80 %), carbon black (15 %) and poly(vinylidene fluoride) (5 %) in N-methyl-2-pyrrolidone. The slurry coated copper foil was dried at 80 °C for 24 hours and then pressed between two stainless steel plates. Coin-type cells of 2025 were assembled in an Ar-filled
glove box with a pure lithium foil as the counter electrode. The two electrodes were separated by a Celgard 2400 membrane and electrolyte containing 1 M LiPF<sub>6</sub> dissolved in ethyl carbonate and diethyl carbonate (1:1, v/v). The charge/discharge performance was tested between 3.00 V and 0.01 V, using the LAND CT2001A multi-channel battery testing system at room temperature. The electrochemical impedance spectra (EIS) measurements were carried out with a BioLogic VMP3 station.
**Fig. S1** TEM images of Fe₃O₄@AG (a), Cit-Fe₃O₄ (b) and Cit-Fe₃O₄@C (c) nanospheres.
Fig. S2 TGA curve of Cit-Fe₃O₄@C nanospheres.

The carbon contents \( W_{\text{carbon}} \) in the N-mFe₃O₄@C and Cit-Fe₃O₄@C nanospheres were calculated from the corresponding TGA results by the following equation.

\[
W_{\text{carbon}} = 100\% - W_r \times \frac{2}{3} \times \left( \frac{M_{\text{Fe}_3\text{O}_4}}{M_{\text{Fe}_2\text{O}_3}} \right) \times 100 \% - W_{\text{water}}
\]

\( W_{\text{water}} \) represents for the weight lose of the adsorbed water at relatively low temperature (around 130 °C). \( W_r \) represents the weight of the residual Fe₂O₃ at 750 °C (all the Fe₃O₄ should be oxidated to Fe₂O₃ at 750 °C). \( M_{\text{Fe}_3\text{O}_4} \) (232 g/mol) and \( M_{\text{Fe}_2\text{O}_3} \) (160 g/mol) are the molar masses of Fe₃O₄ and Fe₂O₃, respectively.
Fig. S3 SEM image and EDX mapping of Fe, C and N elements of the as obtained N-mFe₃O₄@C nanospheres.
**Table S1** the content of elements obtained from XPS analysis

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Fe (wt %)</th>
<th>O (wt %)</th>
<th>C (wt %)</th>
<th>N (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AG</td>
<td>0</td>
<td>42.31</td>
<td>56.56</td>
<td>1.13</td>
</tr>
<tr>
<td>Fe₃O₄@AG</td>
<td>5.94</td>
<td>36.00</td>
<td>55.71</td>
<td>2.35</td>
</tr>
<tr>
<td>N-mFe₃O₄@C</td>
<td>11.68</td>
<td>18.13</td>
<td>65.92</td>
<td>4.27</td>
</tr>
</tbody>
</table>

**Table S2** the elemental analysis results of the carbon species

<table>
<thead>
<tr>
<th>Sample name</th>
<th>C (wt %)</th>
<th>H (wt %)</th>
<th>N (wt %)</th>
<th>O (wt %)</th>
<th>S (wt %)</th>
<th>C:N&lt;sup&gt;d&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>AG-C&lt;sup&gt;a&lt;/sup&gt;</td>
<td>73.45</td>
<td>3.68</td>
<td>0.23</td>
<td>22.54</td>
<td>0.10</td>
<td>372.57:1</td>
</tr>
<tr>
<td>N-mFe₃O₄@C&lt;sup&gt;b&lt;/sup&gt;</td>
<td>58.50</td>
<td>3.68</td>
<td>14.93</td>
<td>22.37</td>
<td>0.52</td>
<td>4.57:1</td>
</tr>
<tr>
<td>Cit-Fe₃O₄@C&lt;sup&gt;b&lt;/sup&gt;</td>
<td>53.38</td>
<td>3.07</td>
<td>17.61</td>
<td>25.75</td>
<td>0.19</td>
<td>3.54:1</td>
</tr>
</tbody>
</table>

a: the sample is obtained by direct pyrolysis of AG at 450 °C in N₂ for 2h.
b: the samples are obtained by etching the Fe₃O₄ away by HCl acid.
c: calculated by deducting the C, H, N and S values from 100 %.
d: mole ratio.
Fig. S4 Pore size distribution curve of the as prepared N-mFe₂O₄@C nanospheres (a); N₂ adsorption-desorption isotherm of Cit-Fe₂O₄@C nanospheres and the corresponding pore size distribution curve (b and c).
**Fig. S5** EIS of the freshly prepared anodes with $\text{N-mFe}_3\text{O}_4@\text{C}$ and $\text{Cit-Fe}_3\text{O}_4@\text{C}$ nanospheres as active materials.