Electronic Supplementary Material (ESI) for RSC Advances

Electronic Supplementary Information (ESI)

Facile fabrication of mesoporous N-doped Fe_3O_4@C nanospheres as superior anodes for Li-ion batteries

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Experimental section

Fabrication of mesoporous N-doped Fe_3O_4@C nanospheres

First, 0.40g arabic gum (AG), 0.65 g $FeCl_3 \cdot 6H_2O$, 0.59 g $Na_3Cit \cdot 2H_2O$, 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 ^oC for 10 hours. After cooling to room temperature, the AG coated magnetic (denoted as Fe_3O_4@AG) nanoparticles were collected by a magnetic bar, washed with ethanol and dried at 60 ^oC. Finally, the Fe_3O_4@AG nanoparticles were annealed at 450 ^oC for 4h under the N_2 atmosphere to give the mesoporous N-doped Fe_3O_4@C (denoted as N-mFe_3O_4@C) nanospheres.

For comparison, the citrate stabilized Fe_3O_4 nanoparticles (denoted as Cit-Fe_3O_4) were also synthesized without adding AG and carbonized (denoted as Cit-Fe_3O_4@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. N_2 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-methy1-2-pyrrolidone. The slurry coated copper foil was dried at 80 ^oC 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 membrance and electrolyte containing 1 M $LiPF_6$ 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.

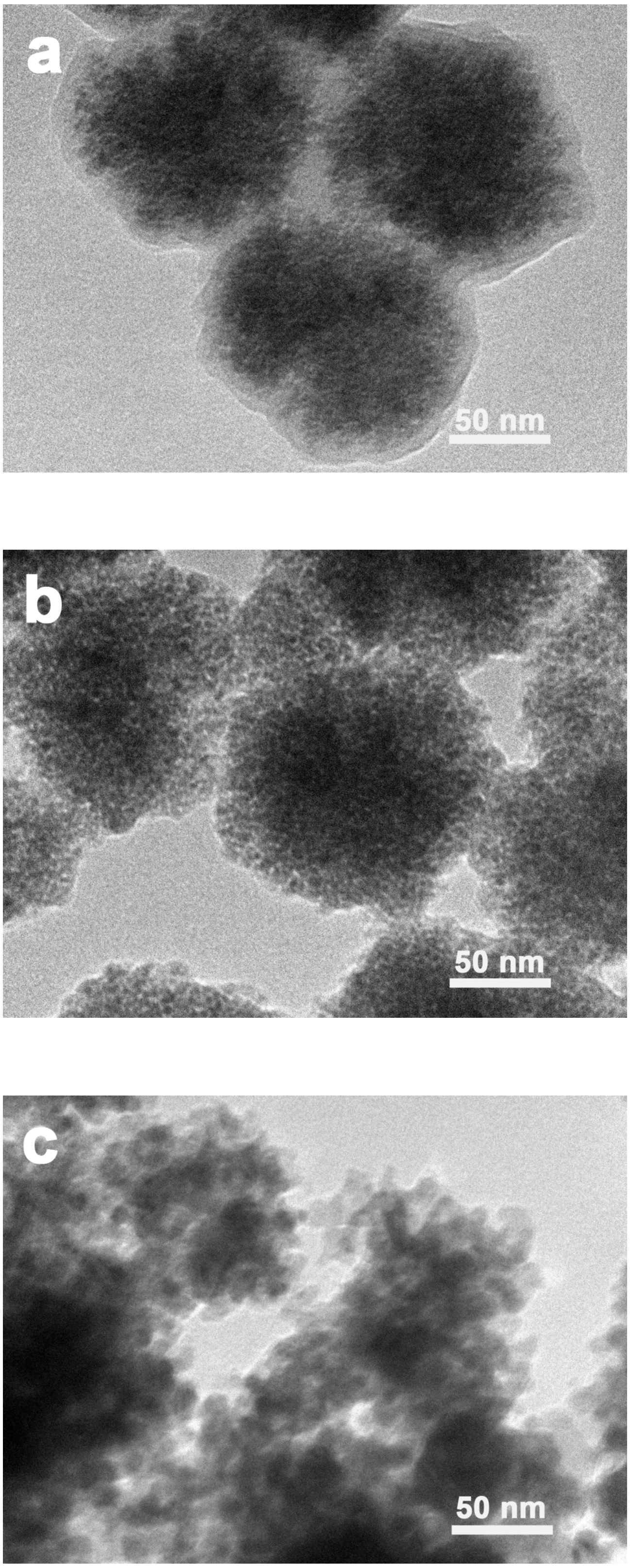

Fig. S1 TEM images of Fe_3O_4@AG (a), Cit-Fe_3O_4 (b) and Cit-Fe_3O_4@C (c) nanospheres.

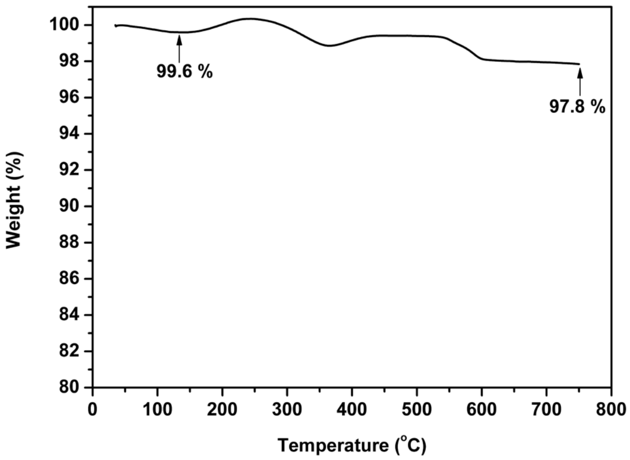

Fig. S2 TGA curve of Cit-Fe_3O_4@C nanospheres.

The carbon contents (W_{carbon}) in the N-mFe_3O_4@C and Cit-Fe_3O_4@C nanospheres were calculated from the corresponding TGA results by the following equation.

$$W_{carbon} = 100\% - W_r \times (2/3) \times (M_{Fe3O4}/M_{Fe2O3}) \times 100\ \% - W_{water}$$

W_{water} represents for the weight lose of the adsorbed water at relatively low temperature (around 130 ^{o}C). W_r represents the weight of the residual Fe_2O_3 at 750 ^{o}C (all the Fe_3O_4 should be oxidated to Fe_2O_3 at 750 ^{o}C). M_{Fe3O4}（232 g/mol） and M_{Fe2O3}（160 g/mol） are the molar masses of Fe_3O_4 and Fe_2O_3, respectively.

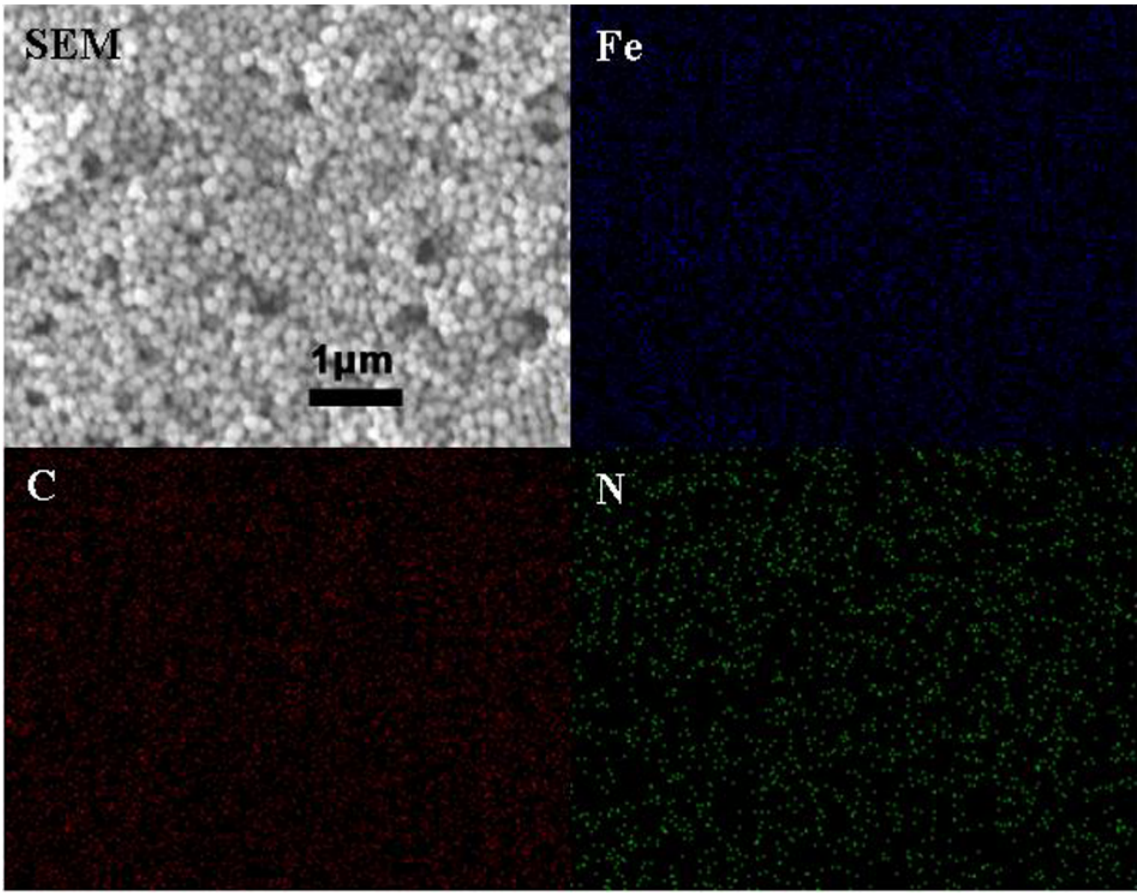

Fig. S3 SEM image and EDX mapping of Fe, C and N elements of the as obtained N-mFe_3O_4@C nanospheres.

Table S1 the content of elements obtained from XPS analysis

Sample name	Fe (wt %)	O (wt %)	C (wt %)	N (wt %)
AG	0	42.31	56.56	1.13
Fe_3O_4@AG	5.94	36.00	55.71	2.35
N-mFe_3O_4@C	11.68	18.13	65.92	4.27

Table S2 the elemental analysis results of the carbon species

Sample name	C (wt %)	H (wt %)	N (wt %)	O (wt %)[c]	S (wt %)	C:N[d]
AG-C[a]	73.45	3.68	0.23	22.54	0.10	372.57:1
N-mFe_3O_4@C[b]	58.50	3.68	14.93	22.37	0.52	4.57:1
Cit-Fe_3O_4@C[b]	53.38	3.07	17.61	25.75	0.19	3.54:1

a: the sample is obtained by direct pyrolysis of AG at 450 °C in N_2 for 2h.

b: the samples are obtained by etching the Fe_3O_4 away by HCl acid.

c: calculated by deducting the C, H, N and S values from 100 %.

d: mole ratio.

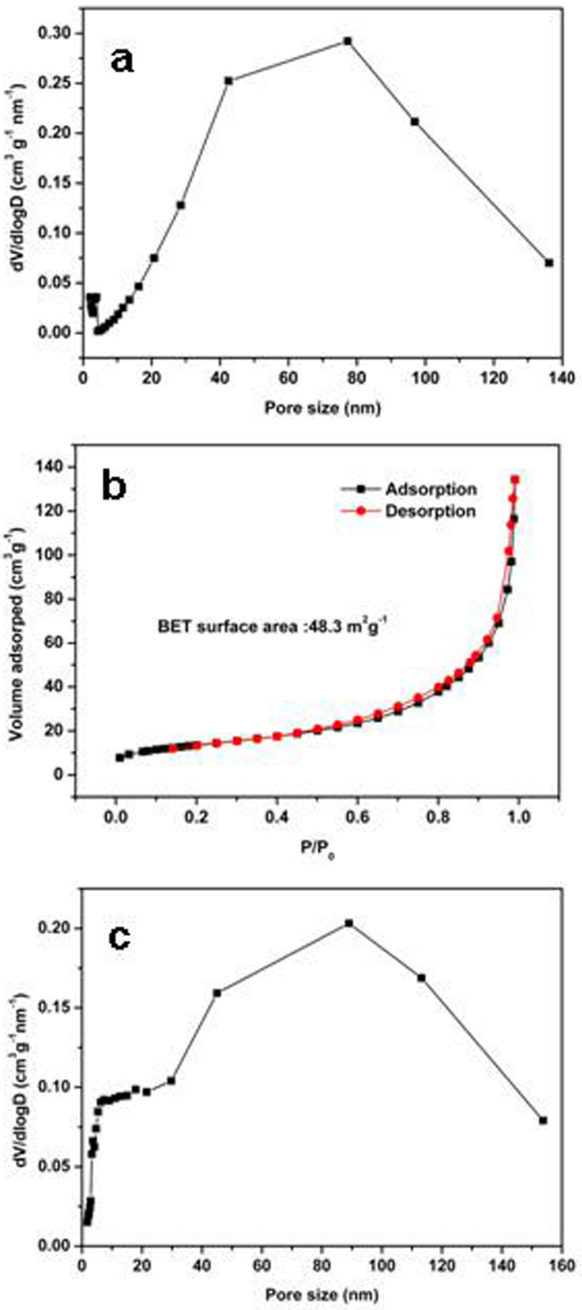

Fig. S4 Pore size distribution curve of the as prepared N-mFe_3O_4@C nanospheres (a); N_2 adsorption-desorption isotherm of Cit-Fe_3O_4@C nanospheres and the corresponding pore size distribution curve (b and c).

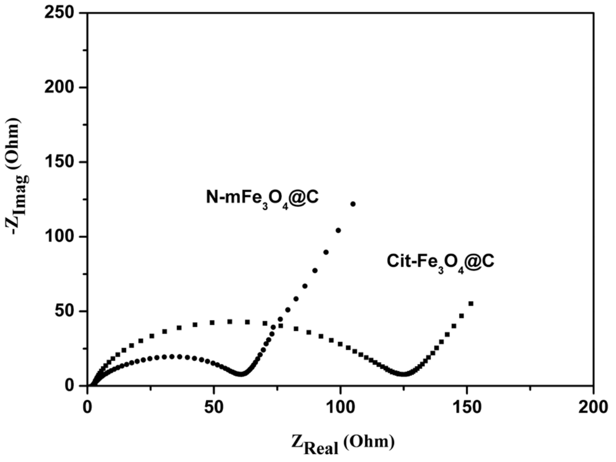

Fig. S5 EIS of the freshly prepared anodes with N-mFe$_3$O$_4$@C and Cit-Fe$_3$O$_4$@C nanospheres as active materials.