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One-step pyrolysis synthesis of octahedral Fe_3O_4/C nanocomposites as superior anode for sodium-ion batteries

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Experimental

Preparation of octahedral Fe_3O_4/C composite

In a typical experimental procedure, polyethylene glycol (15 ml) and ferrous oxalate (1.5 g) were added into a stainless-steel autoclave of 20 ml capacity. The autoclave was sealed and put into an electronic furnace at room temperature. The temperature of the furnace was increased from room temperature to 550 °C in 55 min and maintained at 550 °C for 12 h, and then the autoclave was allowed to cool to room temperature naturally. The dark precipitates in the autoclave were collected and washed with absolute ethanol and distilled water for several times. After that, these products were dried in a vacuum oven at 60 °C for 5 h for further characterization. The overall favorable reaction can be expressed as:

$$FeC_2O_4 + H{-}(O{-}CH_2{-}CH_2)_n{-}OH \rightarrow Fe_3O_4 + C + CO\uparrow + CO_2\uparrow + H_2O\uparrow$$

Characterization

X-ray diffraction (XRD) analysis was performed on a Bruker D8 advanced X-ray diffractometer equipped with graphite-monochromatized Cu-Ka radiation (l = 1.5418 A°). The chemical composition of the sample was analyzed by X-ray photoelectron instruments (XPS, VGESCALABMK X-ray spectrometer). Raman spectrum was recorded on a LABRAM-HR confocal laser MicroRaman spectrometer with an argon-ion laser at an excitation wavelength of 514.5 nm. Inductively coupled plasma (ICP) analysis was carried out on Optima 2000DV. The morphologies of the samples were observed through scanning electron microscopy (SEM) and transmission electron microscope (TEM) measurements, which were carried out on a JEOL JSM-7600F field emission instrument and a JEM 1011 TEM, respectively. High-resolution transmission electron microscope (HRTEM) images were carried out on a JEOL 2100 transmission electron microscope with an accelerating voltage of 200 KV. Thermal gravimetric analysis (TGA) was carried out on a Mettler Toledo TGA/SDTA851 thermal analyzer apparatus under air atmosphere.

Electrochemical measurements

The electrochemical discharge/charge tests of the samples were performed on a Land battery test system (CT2001A). The working electrodes were prepared by pasting a mixed slurry that consisted of 70 wt% active materials (Fe_3O_4/C), 20 wt% carbon black and 10 wt% sodium carboxymethyl cellulose (CMC) on a copper foil. The fabricated working electrodes dried in vacuum oven at 60 ℃ for 24 h. Celgard 2300 microporous polypropylene membrane was used as separator. The electrolyte consisted of a solution of 1 M $NaClO_4$ in an ethylene carbonate/dimethyl carbonate (EC/DMC, 1:1w/w). Sodium foils were used as counter electrodes. The batteries were assembled in an argon-filled glove box and cycled at different current density between voltage limits of 0.01 and 2.5 V. The cyclic voltammetry (CV) test was carried out in the potential window of 0.01 to 2.5 V on an electrochemical workstation (CHI 660e). The electrochemical impedance spectroscopy (EIS) was measured with a Princeton Applied Research. The EIS were carried out by applying an alternating current voltage of 10 mV in the frequency from 10 mHz to 100 kHz at open-circuit voltage before charge/discharge test.

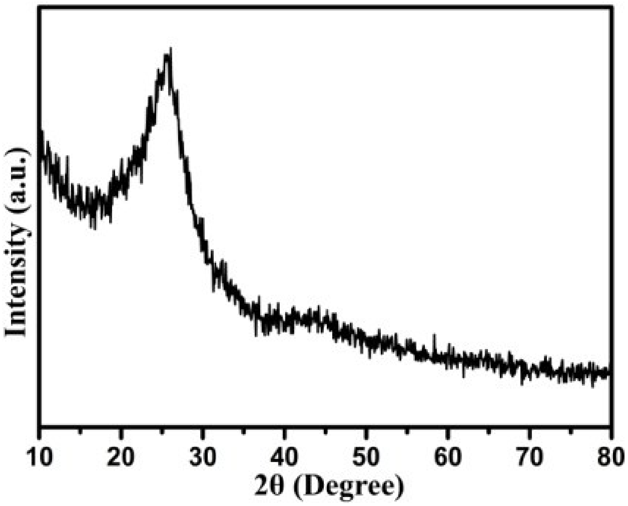

Fig. S1 XPD pattern of the hollow carbon nanocages.

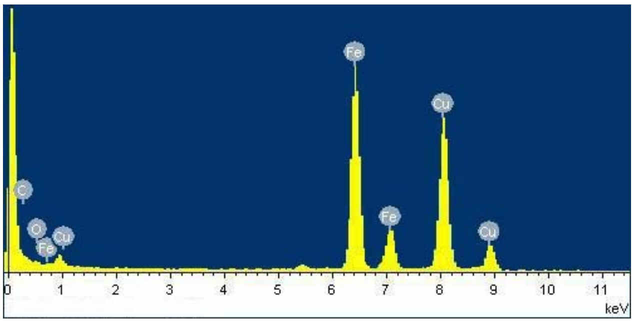

Fig. S2 EDS of the octahedral Fe_3O_4/C nanocomposites.

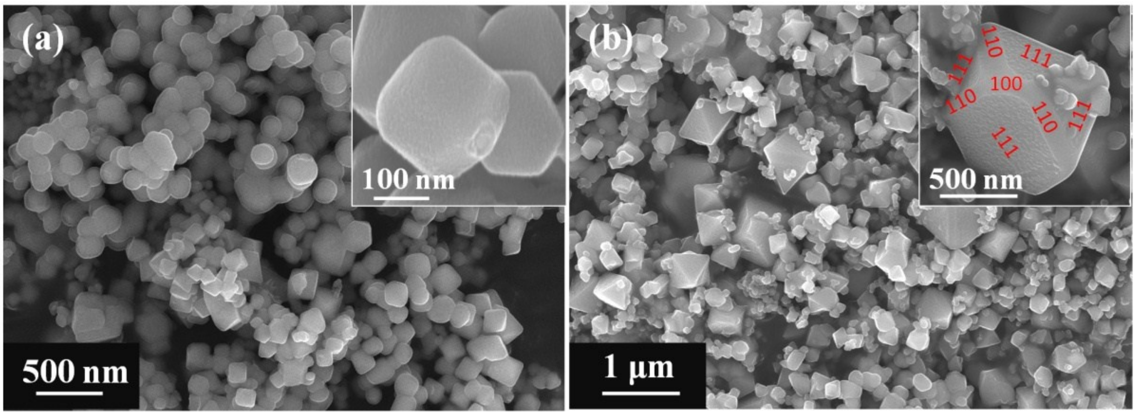

Fig. S3 SEM images of Fe_3O_4/C obtained at 450 ˚C (a) and 650˚C (b).

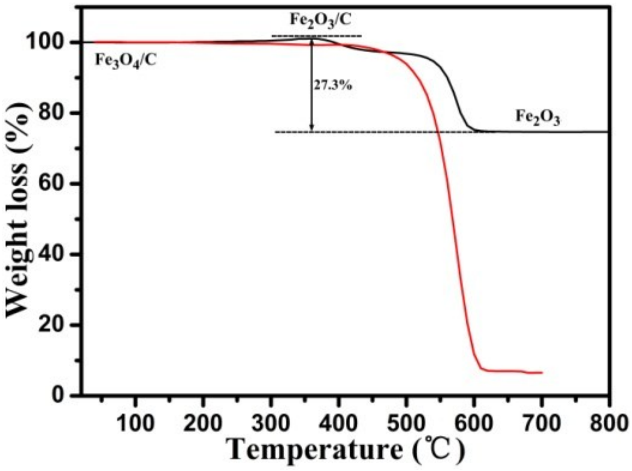

Fig. S4 TGA curves of the Fe_3O_4/C under air atmosphere.

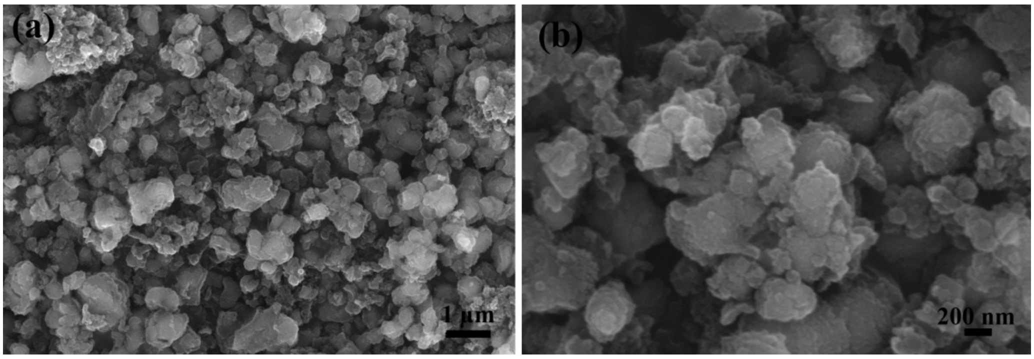

Fig. S5 SEM images of the Fe_3O_4/C electrode after 60 cycles.

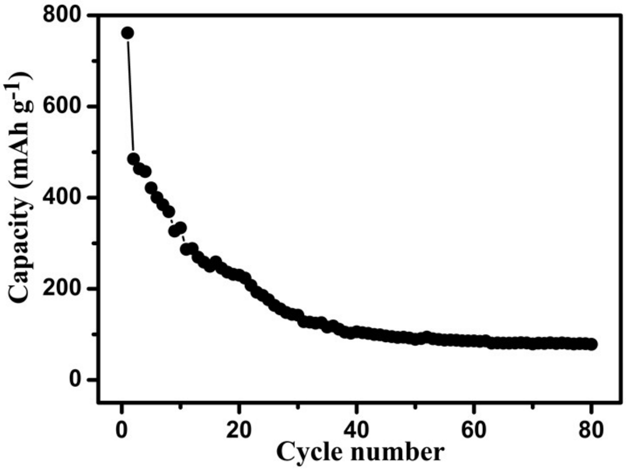

Fig. S6 Cycling performance of the pristine Fe_3O_4 electrode.

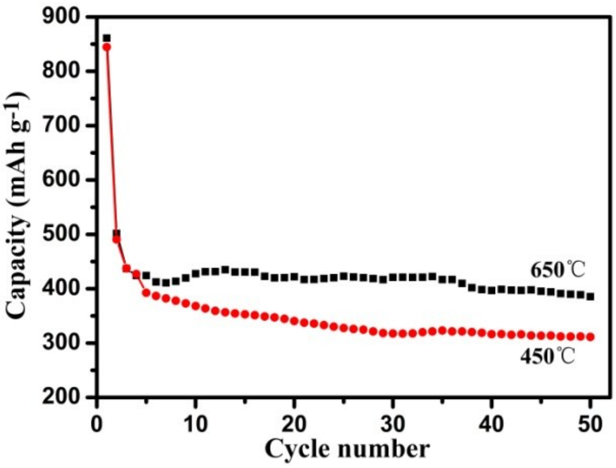

Fig. S7 Cycling performance of the Fe_3O_4/C obtained at 450 °C and 650 °C.