

There have been a number of recent reports describing possible approaches to circumvent the issues posed by the unsatisfactory conductivity, and severe volume change of Fe_3O_4 . One of them is to utilize nanometer-scale particles with designed morphology, such as nanospheres, nanowires, nanorods, nanotubes, and hollow nanostructures, for improving the electrochemical response of the electrodes [4–8]. It is in fact expected that the passage from bulk to nanostructures results in shorter path lengths for lithium ion transport and accommodation of the mechanical strain of lithium ion insertion/extraction. However, there has been limited success in producing Fe_3O_4 nanostructured electrodes with satisfactory high specific capacity and high rate capability. Another effective approach in tackling the above problems is the creation of carbon-based composites containing the active material of Fe_3O_4 . For instance, some groups have synthesized Fe_3O_4 nanospheres with carbon matrix support [9] and carbon-coated Fe_3O_4 nanostructures [10–14] to improve electrochemical performances. The others have employed porous carbon [15–18] or graphene or/and carbon nanotubes [19–24] as substrate materials for synthesis of captive nanoparticles confined in or bonded to the carbon. An advantage of this method is that it is applicable to a variety of metal oxides such as Fe_3O_4 , Fe_2O_3 , NiO and Co_3O_4 , etc. It is hypothesized that the introduced carbon matrices not only function as a structural buffering layer to cushion the mechanical stress caused by the large volume change of Fe_3O_4 during the charge–discharge process, but also act as a robust network to preserve good electronic conductivity of the overall electrode. Although a great success has been achieved in designing and preparing Fe_3O_4 /carbon composites with relatively high specific capacity and cyclability at lower charge/discharge rates when used as anode materials for LIBs, the preparation of Fe_3O_4 /carbon composite electrodes with high specific capacity and cyclability at higher charge/discharge rates remains a great challenge. Recently, Dillon et al. have successfully fabricated a high-rate Li-ion anode based on a nanostructured Fe_3O_4 /SWCNT composite, which was obtained by embedding Fe_3O_4 nanoparticles uniformly in an interconnected single-walled carbon nanotube (SWCNT) net [25]. However, the production of pure SWCNTs is very expensive and difficult to scale up, which is very unfavorable for their wide application in LIBs.

Herein, we report an easy and scalable one-pot hydrothermal process followed by annealing in argon atmosphere using glucose and iron nitrate as source materials to prepare uniform and small Fe_3O_4 nanocrystals encapsulated in interconnected carbon nanospheres (designated as Fe_3O_4 @C nanospheres) for a high-rate LIB anode. This one-pot synthesis approach in situ generates uniform Fe_3O_4 nanocrystals in a confined nanospace of carbonaceous matter, which can obviate the requirement of an additional step to introduce a layer of carbon coating on the surface of the pre-synthesized iron oxide. During the electrochemical measurement, these interconnected Fe_3O_4 @C nanospheres demonstrate excellent cycling performance at 1 C (1 C = 924 mA/g) with a reversible capacity of 784 mA h/g after 50 cycles and superior rate capability, exhibiting 568 and 379 mA h/g at 5 and 10 C, respectively.

2. Experimental

2.1. Synthesis of interconnected Fe_3O_4 @C nanospheres

The reagents were purchased from Tianjin Chemical Reagent Company and used without further purification. In a typical synthesis, 0.9 g glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) was dissolved in 40 mL deionized water and 1.212 g iron (III) nitrate enneahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) was dissolved in 2 mL deionized water. The above two aqueous solutions were then mixed together and ultrasonicated for 15 min. The resulting mixed solution (37.5 mL) was transferred into a 40 mL Teflon-lined stainless steel autoclave, and then heated at 190 °C for 9 h. Once cooled to room temperature naturally, the resulted solid was collected through centrifugation and washed thoroughly with deionized water for several times. Subsequently, the obtained product was redispersed into a certain amount of deionized water, and freeze dried to obtain Fe_2O_3 nanocrystals encapsulated in interconnected carbon nanospheres (designated as Fe_2O_3 @C nanospheres). Finally, the interconnected Fe_2O_3 @C nanospheres were annealed at 500 °C for 2 h in a tube furnace under a flowing Ar atmosphere to obtain Fe_3O_4 nanocrystals encapsulated in interconnected carbon nanospheres (Fe_3O_4 @C nanospheres).

2.2. Characterization of the Fe_2O_3 @C and Fe_3O_4 @C nanospheres

The morphology, dimension, lattice distances, and crystallographic structures of the Fe_2O_3 @C and Fe_3O_4 @C nanospheres were studied by transmission electron microscope (TEM) and high-resolution TEM (HRTEM) performed on a FEI Tecnai G² F20 TEM. Energy-dispersive X-ray spectroscopy (EDX) analyses of a group of Fe_3O_4 @C nanospheres were carried out with spatially resolved EDX spectrum attached to the TEM. Scanning electron microscope (SEM) investigations were performed using a TDCLS-4800 SEM (Hitachi). Raman spectrum of the Fe_3O_4 @C nanospheres was recorded on the LabRAM HR Raman spectrometer using laser excitation at 514.5 nm from an argon ion laser source to validate the presence of carbon in the nanospheres. X-ray diffraction (XRD) measurements were taken on a Rigaku D/max diffractometer with Cu K α radiation at a wavelength of 1.5406 Å, and a step size of 0.02° to characterize the structure of the Fe_2O_3 @C and Fe_3O_4 @C nanospheres. JADE5 software was utilized for data analysis. The crystallite size of nanoparticles is calculated by the Scherrer equation.

$$L = 0.89\lambda / \beta(\theta) \cos \theta$$

where λ is the X-ray wavelength in nm, β is the intrinsic peak width in radians on a 2θ scale, θ is the Bragg diffraction angle, and 0.89 is the Scherrer constant. Thermogravimetric analysis (TGA) was performed with a Perkin Elmer (TA instruments) up to 1000 °C at a heating rate of 10 °C/min in air. N_2 adsorption-desorption isotherms were measured with an autosorb iQ instrument (Quantachrome U.S.) at 77 K. The Brunauer–Emmett–Teller (BET) method was utilized to calculate the specific surface areas. The pore size distributions were derived from the desorption branches of the isotherms based on the Barrett–Joyner–Halanda (BJH) model.