

2.3. Electrochemical measurements

The electrochemical measurements were conducted using coin-type test cell (CR2032) with lithium metal working as both counter and reference electrode. The working electrodes were prepared by the following steps: 80 wt.% active materials ($\text{Fe}_3\text{O}_4\text{@C}$ nanospheres, bare carbon without Fe_3O_4 or commercial Fe_3O_4 nanoparticles with an average diameter of 20 nm purchased from DK nanotechnology Co. LTD, Beijing), 10 wt.% conductivity agent (carbon black) and 10 wt.% binder (polyvinylidene fluoride, PVDF) were blended with N-methylpyrrolidone as a solvent. Electrode film was prepared by coating the mixture on a copper foil and dried successively in a vacuum oven at 80 °C for 4 h first and then 120 °C for 12 h. A Celgard 2400 polypropylene membrane was used as the separator. 1.0 M LiPF_6 in an ethylene carbonate/dimethyl carbonate (EC/DMC/DEC) mixture (1:1:1 v/v/v) was used as the electrolyte. The assembly of the cell was conducted in an argon-filled glove box. Cyclic voltammetry (CV) measurement was conducted at 0.1 mV/s within the range of 0.01–3.0 V on CHI660D electrochemical workstation. Galvanostatic charge/discharge tests were performed on Land CT2001A (China) at different current densities with the potential between 0.005 and 3.00 V (vs. Li/Li^+). All the specific capacities here were calculated on the basis of the total weight of the $\text{Fe}_3\text{O}_4\text{@C}$ nanospheres, the bare carbon or the commercial Fe_3O_4 nanoparticles.

3. Results and discussion

Our novel fabrication process for interconnected $\text{Fe}_3\text{O}_4\text{@C}$ nanospheres principally consists of two steps, as shown in Fig. 1A. The first step involves producing uniform and ultrasmall Fe_2O_3 nanocrystals encapsulated in interconnected carbon nanospheres through hydrothermal treatment on aqueous solution containing iron nitrate (0.075 mol/L) and glucose (0.125 mol/L) at 190 °C for 9 h. It has been reported that when glucose was hydrothermally carbonized at 160–200 °C, carbonaceous spheres of tunable sizes in the nano- to micrometer range were

synthesized. During the hydrothermal process, the glucose molecules underwent dehydration, condensation, or polymerization and aromatization reactions, leading to carbonaceous spheres, which consist of a highly aromatic nucleus (hydrophobic) and a hydrophilic shell containing a high concentration of reactive oxygen functional groups (i.e., hydroxyl/phenolic, carbonyl, or carboxylic) [26,27]. Furthermore, hydrothermal carbonization of glucose in the presence of inorganic salts can give rise to the formation of core/shell metal/carbon hybrid materials (such as Ag@C , Cu@C , Au@C , etc.) [26,28–30]. As for the inorganic salt of iron nitrate, it can be transformed to $\alpha\text{-Fe}_2\text{O}_3$ nanocrystals during the hydrothermal treatment, which are tend to bind with the surface functional groups of the carbon colloids derived from glucose through the Coulombic interaction [31,32]. Inspired by these previous works, we designed a one-pot hydrothermal reaction using glucose and iron nitrate as source materials and successfully produced interconnected carbon nanospheres with uniform and ultrasmall $\alpha\text{-Fe}_2\text{O}_3$ nanocrystals encapsulated (designated as $\text{Fe}_2\text{O}_3\text{@C}$). The speculated formation process of the $\text{Fe}_2\text{O}_3\text{@C}$ nanospheres is shown in Fig. 1B. During the initial stage of the hydrothermal carbonization, dehydration of glucose results in very small carbonaceous colloids with a low degree of polymerization and hydrolysis of iron nitrate leads to FeOOH [31], which further is reduced to uniform $\alpha\text{-Fe}_2\text{O}_3$ nanocrystals by hydrogen released from the carbonization process [33]. The $\alpha\text{-Fe}_2\text{O}_3$ nanocrystals then combine with very small carbonaceous colloids through Coulombic interactions and condense to generate carbon nanospheres with Fe_2O_3 nanocrystals encapsulated. Moreover, it is also found that the size of the carbon nanospheres and the content of the Fe_2O_3 nanocrystals can be tuned by adjusting the experimental parameters, such as the reaction temperature, reaction time and the initial ratio between iron nitrate and glucose. With a lower temperature, shorter time and lower initial ratio of iron nitrate to glucose, smaller carbon nanospheres with less Fe_2O_3 nanocrystals encapsulated can be obtained, as shown in Fig. S1. In the second step, the interconnected $\text{Fe}_2\text{O}_3\text{@C}$ nanospheres are annealed at 500 °C for 2 h in Ar to in situ yield uniform and small Fe_3O_4 nanocrystals

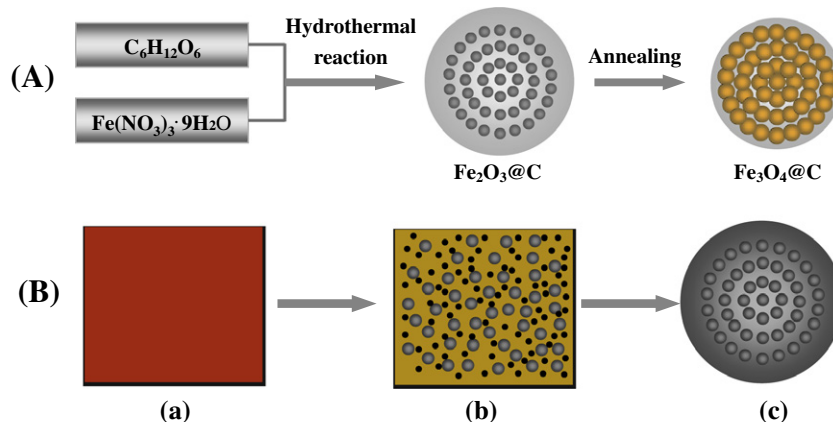


Fig. 1 – Scheme of the formation process of (A) uniform and small Fe_3O_4 nanocrystals encapsulated in the carbon nanosphere and (B) uniform and ultrasmall Fe_2O_3 nanocrystals encapsulated in the carbon nanosphere: (a) aqueous solution of iron nitrate and glucose, (b) iron oxide nanocrystals (gray dots) and small carbonaceous colloids (black dots) formed during the initial stage of the hydrothermal carbonization, (c) carbon nanosphere with uniform and ultrasmall Fe_2O_3 nanocrystals encapsulated.