Controlled Synthesis of Graphene Anchored with Hollow Fe$_2$O$_3$ Nanoparticles for High Lithium Ion Storage

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Transition metal oxides (MOs) have been extensively investigated as anode materials for lithium ion batteries (LIBs) due to their high theoretical capacities (> 600 mAhg$^{-1}$). Among them, iron-based MOs have great potential owing to their high theoretical capacity, low cost, and abundance. However, electrochemical applications of these MOs are hindered by their inherently poor conductivity and capacity fading arising from the large volume change during Li$^{+}$ insertion and extraction.$^{[1,3]}$ In this work, we report a simple, one-step hydrothermal route to synthesize hollow Fe$_2$O$_3$ nanoparticles anchored on graphene sheets. The morphological evolutions of Fe$_2$O$_3$ hollow nanoparticles grown on the graphene sheets, and their electrochemical performance were investigated.

![Figure 1](image-url)  
Figure 1. SEM images of graphene/hollow Fe$_2$O$_3$ nanoparticles synthesized under different reaction time: (a) 6h (Gr-Fe-6), (b) 12h (Gr-Fe-12), (c) 24h (Gr-Fe-24), (d) 48h (Gr-Fe-48).

At the beginning, Fe$_2$O$_3$ solid nanoparticles were grown on the surface of graphene sheets, as the reaction time increased, phosphate ions were adsorbed selectively on the Fe$_2$O$_3$ nanocrystals and dissolved the crystal planes parallel to the $c$ axis other than (0001).$^{[1,5]}$ The Fe$_2$O$_3$ particles were dissolved into hollow structures with small holes in rough surface during the reaction process. After a long reaction time of 48 hours, the final particles appeared with smooth surfaces and a high surface to volume ratio. Such selective absorption of phosphate ions favors the dissolution along the $c$ axis and the formation of the hollow nanostructures. More importantly, the hollow Fe$_2$O$_3$ nanostructures obtained following preferential dissolution process exhibit superior lithium ion storage.

![Figure 2](image-url)  
Figure 2. (a) Electrochemical performances of Gr-Fe composites electrode at various current rates of 0.1, 0.3, 0.5, 1, 2, 3 Ag$^{-1}$; (b) Capacity performances of Gr-Fe-24 at current rates of 0.1 and 2 Ag$^{-1}$ for 90 cycles and 700 cycles, respectively. All capacities are calculated on the basis of the total mass of the hybrid materials in this work.

The cycle retention and capacity performance of Gr-Fe-24 anode were further evaluated at 0.1 Ag$^{-1}$ for 90 cycles, and at 2 Ag$^{-1}$ for 700 cycles, respectively. An impressive capacity of 877 mAhg$^{-1}$ at 0.1 Ag$^{-1}$ can be maintained for 90 cycles. Furthermore, the reversible discharge capacity of Gr-Fe-24 electrode can sustain 285 mAhg$^{-1}$ after 700 cycles under a high current density of 2 Ag$^{-1}$ with nearly 100% Coulombic efficiency. These results can be attributed to the small holes in the rough surface of the hollow Fe$_2$O$_3$ nanoparticles and flexible graphene sheets could improve the cycle retention and reversibility of composites electrodes.

References