

to investigate the electrochemical details when the cell was set to be scanned at 0.1 mV/s within the voltage window of 0.01–3.00 V (vs. Li/Li⁺). The patterns are consistent with the CV results from other reports on Fe₃O₄-C composites [13,15–19]. Two cathodic peaks at voltage potentials of 0.97 and 0.68 V are observed in the first cathodic scan, while they disappeared in the following scans, which is due to the irreversible formation of a solid electrolyte interface (SEI) and the decomposition of electrolyte [13,15–19]. In subsequent cycles, the cathodic peak shifts to 0.83 V and tends to be stable, indicating the high Coulombic efficiency and the stable and good reversibility of the sample. In the anodic scans, two small peaks at 1.62 and 1.88 V are recorded. These cathodic and anodic peaks correspond to the electrochemical reduction/oxidation (Fe₃O₄ ↔ Fe) reactions accompanying Lithium ion insertion (lithiation) and extraction (delithiation) [13,15–19].

Fig. 5(b) presents the charge/discharge profiles of the Fe₃O₄@C nanospheres in the 1st, 2nd, 10th, 20th, 30th, 40th, and 50th cycles at a current density of 924 mA/g. The first discharge capacity is 1528 mA h/g, but the first charge capacity is 1096 mA h/g, leading to a relatively low Coulombic efficiency of 71.7%. The relatively low initial Coulombic efficiency may be caused by the irreversible capacity loss, including inevitable formation of SEI and decomposition of electrolyte, which are common to most anode materials [9–24]. This characteristic also agrees well with the CV result that the cathodic peaks are present in the first scan while absent afterward. The discharge voltage plateau at ~0.84 V in the first cycle is different

from those of other cycles at ~1.0 V, further indicating that irreversible reactions occurred in the first cycle. In the second cycle, the Coulombic efficiency increases to 94.2% and a discharge capacity of 1087 mA h/g is achieved (as shown in Fig. 5(c)), which is higher than the theoretical value for Fe₃O₄ (924 mA h/g). Similar results have been reported for many other transition metal oxides [35,36]. It is reported that the reaction of oxygen-containing functional groups on carbon with lithium ions can also contribute to the lithium storage capacity [20,11]. Besides, the reversible decomposition of the electrolyte with the formation of SEI and extra lithium ion adsorption/desorption on the SEI while cycling may lead to the high experimental lithium storage capacity, as well [4]. Note that the charge curve is a sloping curve with no obvious voltage platform, owing to the large surface area induced during the former discharge process which could widen the reaction site energy range for intercalation compounds, [37,38] or the amorphous character of the active materials itself [39].

The comparative cycling performance between the Fe₃O₄@C nanospheres and commercial Fe₃O₄ nanoparticles at a current density of 924 mA/g is illustrated in Fig. 5(c). Apparently, the Fe₃O₄@C sample demonstrates a much better cyclic retention than the commercial Fe₃O₄ nanoparticles, with a high reversible capacity of 811 mA h/g after 20 cycles and 784 mA h/g even after 50 cycles. Furthermore, their Coulombic efficiency is maintained at ~99% after the 12th cycle. For the commercial Fe₃O₄ nanoparticles with average diameter of about 20 nm, their capacity fades very rapidly during the

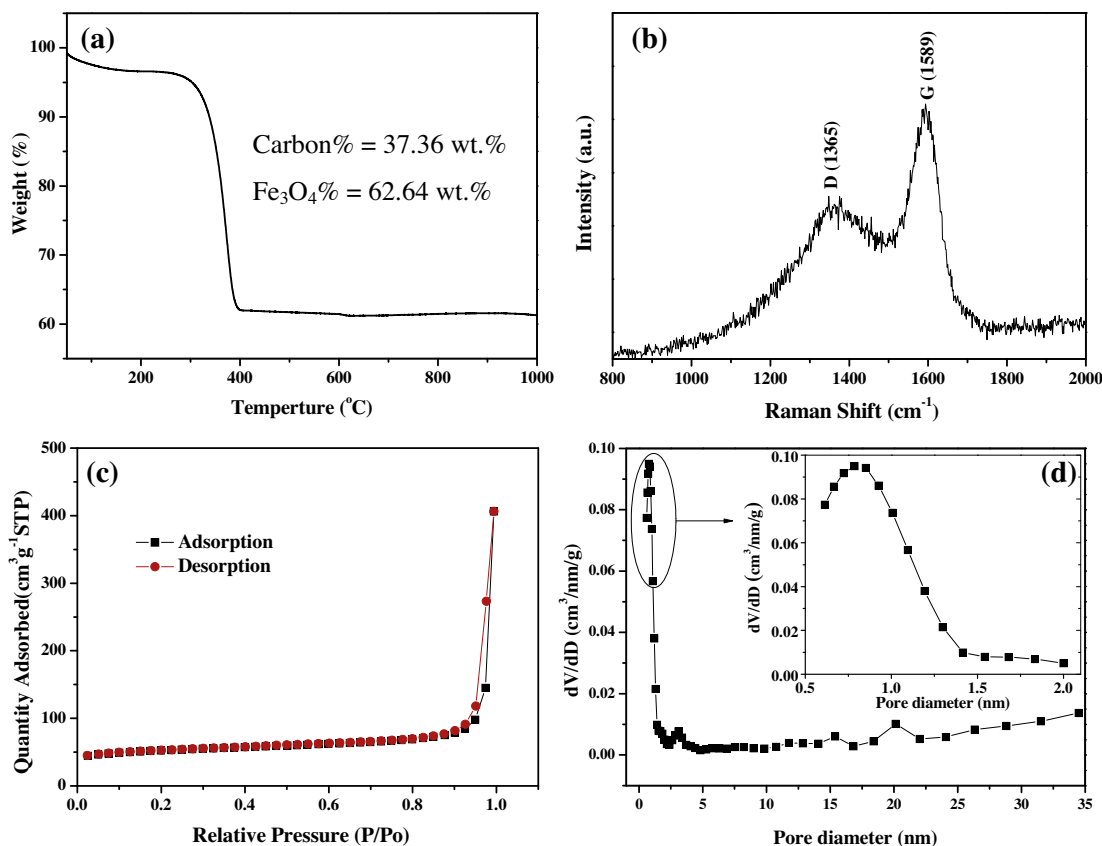


Fig. 4 – (a) TGA curve, (b) Raman spectrum, (c) nitrogen adsorption-desorption isotherms and (d) pore size distribution curve of the Fe₃O₄@C nanospheres, inset of (d) magnification of pore size distribution between 0.5 and 2.0 nm.