



# Study on electrochemical performance of multi-wall carbon nanotubes coated by iron oxide nanoparticles as advanced electrode materials for supercapacitors



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## ABSTRACT

Iron oxide was deposited on surface of multi-walled carbon nanotubes (Fe<sub>2</sub>O<sub>3</sub>@MWNTs) by atomic layer deposition (ALD). By a following calcination process, the electrochemical performance of the Fe<sub>2</sub>O<sub>3</sub>@MWNTs nanocomposites was further improved. From the X-ray diffraction and Raman spectra analysis of nanocomposites, Fe<sub>2</sub>O<sub>3</sub> nanocrystallites were found to be successfully formed after a simple calcination process. The transmission electron microscopy revealed that Fe<sub>2</sub>O<sub>3</sub> nanoparticles with the size of less than 10 nm are uniformly anchored on the surface of MWNTs. The X-ray photoelectron spectroscopy further confirmed that the valence state of iron in the composites is +3 and no other impurities were detected. The Fe<sub>2</sub>O<sub>3</sub>@MWNTs nanocomposites were investigated as electrode materials for high-performance supercapacitor. Electrochemical test results exhibited a high specific capacitance with 787 F g<sup>-1</sup> at a discharge current density of 1 A g<sup>-1</sup> and an outstanding rate performance (72% capacitance retention at 30 A g<sup>-1</sup>), and even after 5000 cycles the capacity retention was still maintained at 91.6%.

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## 1. Introduction

In the past few years, energy security has emerged as one of the topmost global concerns, due to the population growth and increasing emission of greenhouse gases. It is therefore critical for humankind to find alternative energy sources that are renewable and clean to bridge the gap between the increasing energy demand and the climate change. As a result, energy storage and conversion devices, including fuel cells, batteries and electrochemical supercapacitors (ES), have attracted researchers a great deal of attention in recent years [1–5]. They operate under a similar electrochemistry principle and electrochemistry potential difference across two electrodes serves as the energy source for power output. While batteries and fuel cells couple two reactions (oxidation of metal or organic fuel molecules and reduction of electronegative metal oxides or oxygen gas) for energy conversion. ES are a new type of energy storage devices which functions between rechargeable batteries and electrolytic capacitors. Such supercapacitor stores energy through electrostatic charge accumulation at the electrode/

electrolyte interfaces (electrochemical double layer capacitors) and/or through very fast and reversible redox reactions on the electrode interface (pseudo-capacitors). Based on this type of working principles, the ES features much higher capacitances and energy density than electrolytic capacitors, and higher power density than rechargeable batteries [6–8]. With its quick charge-discharge capability, pollution-free and excellent cyclability, ES will be a kind of green energy source for the coming centuries. A typical supercapacitor consists of two electrodes, one collector, one electrolyte and one separator, in which the electrode materials are the critical element to determinate the performance and cost of the device [9,10]. Thus, exploring high-performance and low-cost electrode material is always of the key interest in supercapacitor development and applications.

At present, electrode materials mainly include carbon materials [11–15], metal oxides and hydroxides [16–18] and conductive polymer [19–21]. Metal oxides occupy a significant position in the electrode materials, since its high levels of charge storage in theory. Over the past years, there are a lot of researches on metal oxides served as supercapacitor electrode materials, such as RuO<sub>2</sub>, MnO<sub>2</sub>, NiO, TiO<sub>2</sub>, Co<sub>3</sub>O<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub> and so forth [22–28]. Among these electrode materials, there is growing concern about hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) thanks to its low cost, non-toxicity, earth-abundant and large

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theoretical capacitance [29–31]. Unfortunately, in many cases its capacitance performance, cyclability and rate performance are largely limited to the disadvantages of the low electric conductivity of pure iron oxides in practice. Hence, improving its conductivity has becoming more and more imperative. Several strategies have been explored to achieve better performance for iron-based supercapacitor electrodes, for instance, nanoscale iron oxides materials, including nanoparticles [32], nanotubes [29], nanowires [33], nanoflakes [34] and hollowed nanospheres [21]. On the basis, it is an effective approach to combine nanoscale iron oxides with high conductive carbonaceous materials to achieve desired electrochemical performance. For example, Liu et al. [35] demonstrated a one-step solvothermal method to synthesize  $\text{Fe}_2\text{O}_3$  nanodots anchored on nitrogen-doped graphene sheets, which displays superior capacitance retention after 100000 cycles (about 75.3% at  $5 \text{ A g}^{-1}$ ), providing the best reported long-term cycling stability for iron oxides to date. Chen et al. [36] fabricated graphene/porous  $\text{Fe}_2\text{O}_3$  nanocomposites via a template-assisted nanocasting process, which showed a high specific capacitance and rate capability, but a non-ideal cycling stability (72.3% capacitance retained after 1000 cycle tests).

Carbon nanotubes (CNTs) with the advantages of unique hollow and layered structure, high specific surface area, excellent electrical conductivity, high chemical stabilities and suitable ion transport gaps, have become good carriers for metal oxides.

Earlier research has suggested that introducing metal oxides into CNTs is an effective strategy to achieve improved capacitance, cyclability and rate performance [37–39]. Therefore, introducing  $\text{Fe}_2\text{O}_3$  into CNTs as high-performance electrode materials has great significance for achieving maximum utilization of the  $\text{Fe}_2\text{O}_3$ . Various nanofabrication technologies have been adopted to synthesize the  $\text{Fe}_2\text{O}_3/\text{CNTs}$  nanocomposites, including hydrothermal method [40], chemical vapor deposition (CVD) [41], electrodeposition [42], etc. However, there are obvious drawbacks of these methods, such as low-purity products, nonuniform coating, and high reaction temperature. These drawbacks decrease its performances, and the dissatisfactory capacitance limits its practical application in supercapacitors as well, which pushed us to explore the fabrication of  $\text{Fe}_2\text{O}_3/\text{CNTs}$  composites with a high-purity and high-uniformity  $\text{Fe}_2\text{O}_3$  layer. Yet the atomic layer deposition (ALD) is considered a powerful technique for conformal coating on high-aspect ratio structures since its emergence in the 1970s [43–45], because it could provide more advantages including thickness control at the atomic level, excellent conformity for complex structures, very good uniformity with large scale of thin films, and very low growth temperature [46]. Earlier studies have fulfilled the ALD of  $\text{Fe}_2\text{O}_3$  with various nanostructures, such as  $\text{Fe}_2\text{O}_3$  thin films on silicon wafer [47],  $\text{Fe}_2\text{O}_3$  nanotubes via porous template-directed routes [48] and  $\text{Fe}_2\text{O}_3$  decorated carbon [10]. However, there have been few efforts to conduct a research on  $\text{Fe}_2\text{O}_3/\text{CNTs}$  which are synthesized via ALD as electrode material for supercapacitors. Thus it is very necessary to fabricate the  $\text{Fe}_2\text{O}_3/\text{CNTs}$  composites with a suitable  $\text{Fe}_2\text{O}_3$  loading by ALD for further improving electrochemical performance.

In this study, we designed a nanocomposite architecture where a mass of  $\text{Fe}_2\text{O}_3$  uniformly deposited on the surface of multi-wall carbon nanotubes (MWNTs) by atomic layer deposition (ALD). Subsequently, a simple calcination process was adopted to improve the electrochemical performance of the  $\text{Fe}_2\text{O}_3/\text{MWNTs}$ . Then through adjusting the amount of  $\text{Fe}_2\text{O}_3$  deposited, the electrochemical performance was further optimized. The amount of  $\text{Fe}_2\text{O}_3$  deposited can be controlled precisely by changing the cycle number of ALD [49]. This typical architecture ( $\text{Fe}_2\text{O}_3/\text{MWNTs}$ ) realized the optimality of electrochemical performance of the nanocomposites. The  $\text{Fe}_2\text{O}_3/\text{MWNTs}$  demonstrated high specific capacitance and

outstanding rate capability, due to the synergistic effects coming from  $\text{Fe}_2\text{O}_3$  nanoparticles (high theoretical capacity) and MWNTs (high conductivity and high surface area). In addition, because the  $\text{Fe}_2\text{O}_3$  crystallinity was increased by a simple calcination process, the  $\text{Fe}_2\text{O}_3$  nanocrystallites were formed. The electrochemical results showed that the calcination process effectively improve the electrochemical performance of the  $\text{Fe}_2\text{O}_3/\text{MWNTs}$  nanocomposites.

## 2. Experimental

### 2.1. Materials

Commercial MWNTs (Purity: >98%, SSA: >110  $\text{m}^2 \text{ g}^{-1}$ , Thomas Swan & Co. Ltd) with diameter of 15–18 nm and length of 20  $\mu\text{m}$  were used for experiments. The ALD- $\text{Fe}_2\text{O}_3$  process was carried out in a commercial ALD reactor (Angstrom Dep II, Angstrom Sciences Inc., USA). Prior to ALD, the MWNTs were added into ethanol and ultra-sonicated for 30 min to produce MWNTs dispersion and then dropped onto a quartz wafer, natural drying. Ferrocene ( $\text{FeCp}_2$ ) and ozone ( $\text{O}_3$ ) were used as the metal and oxidative precursors. Prior to deposition, ferrocene as the iron source was heated to 110  $^\circ\text{C}$ , and then deposition temperature was maintain at 250  $^\circ\text{C}$ . The ALD reactor was kept at process pressure of around 0.3 Torr with 40 sccm nitrogen ( $\text{N}_2$ ) flowing as a carrier and purging gas. For comparison, the three groups of samples were prepared with ALD cycles of 800, 1000 and 1200 respectively (noted as 800 $\text{Fe}_2\text{O}_3/\text{MWNTs}$ , 1000 $\text{Fe}_2\text{O}_3/\text{MWNTs}$  and 1200 $\text{Fe}_2\text{O}_3/\text{MWNTs}$ ). After the ALD process, half of per group samples were transferred to a furnace and then calcinated at 400  $^\circ\text{C}$  for 0.5 h (noted as C-800 $\text{Fe}_2\text{O}_3/\text{MWNTs}$ , C-1000 $\text{Fe}_2\text{O}_3/\text{MWNTs}$  and C-1200 $\text{Fe}_2\text{O}_3/\text{MWNTs}$ ). Finally, samples were collected in EP tubes.

### 2.2. Samples characterization

The morphology and microstructure of samples were characterized by transmission electron microscope (TEM; Tecnai G2 20 S-Twin, FEI, Czech Republic). The crystal structure of samples was identified by X-ray diffraction (XRD; 3014-Z2, Rigaku Corporation, Japan) with a scan rate of  $10^\circ \text{ min}^{-1}$ , operating at 40 kV and 30 mA. The crystallinity of  $\text{Fe}_2\text{O}_3$  nanoparticles deposited on MWNTs was determined by Raman spectroscopy (LabRAM HR800, Horiba Scientific, France). The chemical composition of the  $\text{Fe}_2\text{O}_3/\text{MWNTs}$  composite was investigated by X-ray photoelectron spectroscopy (XPS, ESCALab250Xi, Thermo Scientific, USA).

### 2.3. Electrode preparation and electrochemical measurements

Nickel foam was used as the current collector for electrodes. The process of the preparation of working electrodes is as followed: the  $\text{Fe}_2\text{O}_3/\text{MWNTs}$  composites are mixed with acetylene black conductor and polyvinylidene fluoride (PVDF) binder at a weight ratio of 8.5:1:0.5 to form the homogeneous slurry, and then pasted onto a nickel foam ( $1 \times 1 \text{ cm}^2$ ) current collector and dried at 40  $^\circ\text{C}$ , under vacuum for 12 h. The massloading of active materials is about 1 mg for all electrodes. The obtained electrodes were pressed at 5 MP before electrochemical tests.

The electrochemical tests were carried out on an electrochemical workstation (CHI660e, China) using a three-electrode system. The as-obtained electrode, platinum plate,  $\text{Hg}/\text{Hg}_2\text{Cl}_2$  electrode and 3 M KOH aqueous solution as working electrode, counter electrode, reference electrode and electrolyte respectively. Cyclic voltammetry (CV) and galvanostatic charge/discharge (GCD) tests were taken at different scan rates and current densities. Electrochemical impedance spectra (EIS) were collected with

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