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Binder-free, self-standing films of iron oxide nanoparticles deposited on ionic liquid functionalized carbon nanotubes for lithium-ion battery anodes

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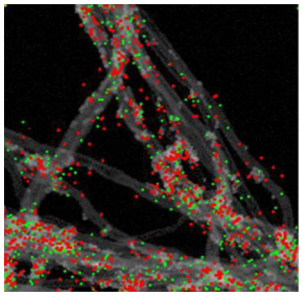
HIGHLIGHTS

- Fe_2O_3 nanoparticles were uniformly deposited onto fCNT via a hydrothermal method.
- LIBs were prepared using a binder-free freestanding electrode.
- ILs improved processability and solubility of CNTs.
- Interactions with ILs preserved the inherently electronic structures of CNTs.
- The capacity of the fCNT/Fe_2O_3 composite was higher than those of CNT and fCNT.

GRAPHICAL ABSTRACT



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ABSTRACT

We report in-situ synthesis and direct deposition of Fe_2O_3 nanoparticles (NPs) on the ionic liquid (IL)-functionalized carbon nanotubes (fCNT). As shown in transmission electron microscope (TEM) and scanning TEM (STEM) images, Fe_2O_3 NPs with the diameter of 3–5 nm are randomly distributed on the sidewall of fCNT, revealing the nanocrystalline structure. The chemical identity and interaction of the fCNT/Fe_2O_3 composite are investigated by FT-IR, Raman and XPS analyses. In particular, the fCNT/Fe_2O_3 composite is solution-processable in a form of binder free and self-standing film. Such a free-standing electrode film based on the fCNT/Fe_2O_3 composite achieve the discharge capacity of 413 mAh g^{-1} which is much greater than 34 mAh g^{-1} of the CNT and 191 mAh g^{-1} of the fCNT due to the redox reaction of Fe_2O_3 NPs. Moreover, the fCNT/Fe_2O_3 composite show the coulombic efficiency of 98% and the capacity fading from 272 mAh g^{-1} to 182 mAh g^{-1} after 50 cycles of charge/discharge.

1. Introduction

Lithium-ion batteries (LIBs) have received significant attention due to high energy density for applications in electrical vehicles, electronic and portable device, and grid technology [1,2]. Although graphite has been used for three decades as a commercial anode material, its specific capacity was limited to 372 mAh g^{-1} of theoretical value [3]. Carbon nanotubes (CNT) are regarded as a potential anode due to large surface area, good electrical property, (electro)chemical and mechanical stabilities, but they also have a critical challenge of the unsatisfactory capacity and low processability arising from van der Waals interactions among tubes [4,5].

Among various transition metal oxides such as TiO_2, SnO_2, MnO_2, and CuO, ZnO that can be used as an alternative anode of commercial graphite for the enhanced specific capacity [6–11], Fe_2O_3 is considered as an attractive electrode material because of

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high theoretical capacity of 1005 mAh g^{-1}, environmental friendliness, abundance, and low cost [12–14]. Carbon nanomaterial/transition metal oxide composite may be the good combination to overcome the limitation of each material by synergizing their advantageous features.

Ionic liquids (ILs) are molten salts in liquid state at room temperature, consisted of organic ions and have unique properties including high ionic conductivity, non-volatile and non-flammable natures, and high chemical and thermal stabilities [15–17]. In particular, ILs have been utilized to modify the physicochemical properties of carbon nanomaterials such as graphene and CNTs, thereby creating emerging soft hybrid materials due to their unique characteristics as demonstrated by us and other groups [18–20]. In a soft hybrid system, ILs can be adsorbed on the carbon nanomaterials via van der Waals and $\pi-\pi$ interactions, leading to the enhancement in their mechanical and chemical properties as well as improving their processability [21].

In this research, we demonstrated binder-free, self-standing anode films prepared by Fe_2O_3 nanoparticle-deposited on IL-functionalized CNT (fCNT) composite. The fCNT acted as the free-standing conductive networks to improve electrical conductivity and mechanical integrity of active Fe_2O_3 and to reduce the total mass of electrode by avoiding the use of any additive and binder for higher specific capacity. The well-defined nanostructure of Fe_2O_3 was constructed on the surface of the fCNT, where ILs played a role of dispersing CNT for large accessible surface area and of providing a favorable interface between CNT and Fe_2O_3 as previously literature [17,22]. The fCNT/Fe_2O_3 composite anodes greatly improved the capacity of the CNT and fCNT because of the redox behavior of Fe_2O_3 NPs.

2. Experimental section

2.1. Fabrication of binder-free, self-standing fCNT/Fe_2O_3 composite films

To fabricate the fCNTs, pristine MWCNT (supplied by Hanwha nanotech) and 1-butyl-3-methylimidazolium tetrafluoroborate ($BMimBF_4$ used as ILs and supplied by MERCK) were first ground at least for 20 min in an agate mortar. The resultant mixture was washed by acetonitrile and deionized (DI) water at several times to remove excess ILs and then, was dried under vacuum.

The fCNT/Fe_2O_3 composites were prepared by a simple solution method. 10 mg of fCNT was dissolved in 16.6 mL of aqueous ethylene glycol solution (ethylene glycol: water = 3:2 v/v). This mixture was sonicated for 1 h (Branson 1510). 1.4 mmol of iron (II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$, Aldrich, 99%) was added into CNT/IL solution. After stirring for 4 h at room temperature, the resulting mixture was heated at 140 °C for 8 h. The final product was washed by DI water and then, filtrated through an anodic aluminum oxide (AAO) membrane filter (47-mm diameter, 0.2-μm pore size, Whatman) under vacuum to obtain a binder-free, self-standing film. Pristine CNT (10 mg) as a control sample was dispersed in 20 mL of dimethylformamide (DMF) with an ultrasonication for 4 h, and then was filtered through AAO membrane filter under vacuum. The filter was dissolved by soaking in high concentration NaOH aqueous solution. The CNT film was transferred to Cu foil and washed with deionized water until pH 7. The resultant film was dried overnight in a vacuum oven.

2.2. Electrochemical measurements

The electrochemical properties of the fCNT/Fe_2O_3 as anode materials were measured by a galvanostatic charge–discharge system. The coin-type cells were assembled in a glove box filled with argon gas. The electrolyte was a solution of 1 M lithium hexafluorophosphate ($LiPF_6$) in ethyl carbonate (EC)/dimethyl carbonate (DMC)/diethyl carbonate (DEC) (1:2:1 in v/v). Li metal was used as the counter and reference electrode. The cells were discharged and charged galvanostatically in the voltage range from 0.01 to 3.0 V (vs. Li^+/Li) at room temperature using a battery cycler (WonAtech, WBCS3000).

2.3. Characterization

The morphology and crystal structure surface were confirmed using a Transmission electron microscopy (TEM). TEM images were taken with a JEM-2100F, Cs corrector (JEOL/CEOS) microscope operated at 200 keV. FT IR spectra were taken Nicolet5700. Each spectrum was recorded from 4000 to 450 cm^{-1}. Raman spectroscopy was measured on a Jobin Yvon/HORIBA spectrometer equipped with charge-coupled device (CCD) camera (1024 × 256 pixels). The X-ray photoelectron spectroscopy (XPS; AXIS-NOVA, Kratos. Inc) was employed to identify the chemical bonding states of the fCNT/Fe_2O_3 composite, monochromatic Al Ka(alpha) (hv = 1486.6 eV) as a radiation source. Thermogravimetric analysis (TGA) was carried out on a TGA Q5000 IR instrument from 50 to 800 °C at a heating rate of 10 °C min^{-1} in air.

3. Results and discussion

The binder-free, free-standing films consisting of Fe_2O_3 NPs-deposited fCNT were readily fabricated through solution chemistry and vacuum filtration (Fig. 1). The fCNT/Fe_2O_3 composites were dispersed in organic polar solvents and solution processable. The film consolidation of the fCNT/Fe_2O_3 composites was achieved as a consequence of the interconnected networking structure and good processability of fCNT. These free-standing conductive films fabricated without using any additive and binder are beneficial for the application in electrode materials because the specific capacity can be improved by reducing the total mass of electrode [23].

As shown in TEM images of Fig. 2, the Fe_2O_3 NPs were randomly distributed on the surface of the fCNT. The existence of Fe_2O_3 on the surface of fCNT was obviously confirmed by a contrast difference due to electron density discrepancy of fCNT and Fe_2O_3. Accordingly,

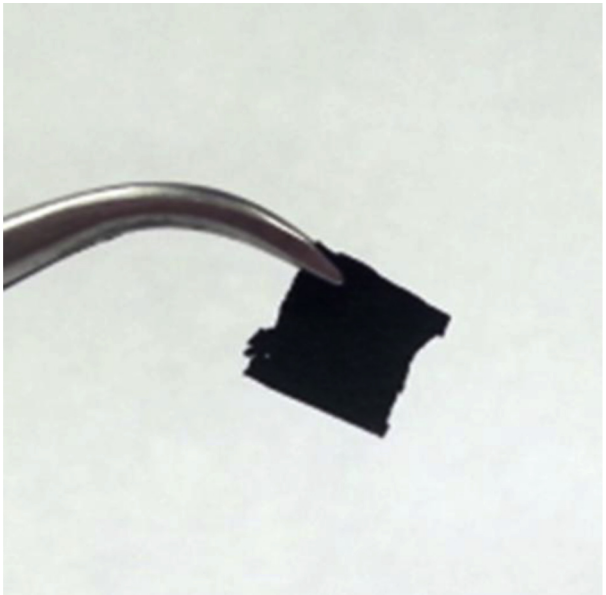

Fig. 1. The binder-free, free-standing film consisting of Fe_2O_3 NP-deposited fCNT.