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Nickel/carbon core/shell nanotubes: Lanthanum nickel alloy catalyzed synthesis, characterization and studies on their ferromagnetic and lithium-ion storage properties

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ABSTRACT

A method was developed to synthesize ferromagnetic nickel core/carbon shell nanotubes (Ni/CNTs) by chemical vapor deposition using Pauli paramagnetic lanthanum nickel ($LaNi_5$) alloy both as a catalyst and as a source for the Ni-core. The Ni-core was obtained through oxidative dissociation followed by hydrogen reduction during the catalytic growth of the CNTs. Transmission electron microscopy (TEM), selected area electron diffraction (SAED) and X-ray diffraction (XRD) analyses reveal that the Ni-core exists as a face centered cubic single crystal. The magnetic hysteresis loop of Ni/CNTs particle shows increased coercivity (446.42 Oe) than bulk Ni at room temperature. Furthermore, the Ni/CNTs core/shell particles were investigated as anode materials in lithium-ion batteries. The Ni/CNTs electrode delivered a high discharge capacity of 309 mA h g^{-1} at 0.2 C, and a stable cycle-life, which is attributed to high structural stability of Ni/CNTs electrode during electrochemical lithium-ion insertion and de-insertion redox reactions.

1. Introduction

New class of hybrid materials like metal/carbon nanocomposites has attracted great attention in the fields of photochemical, optics and electrochemical devices due to the synergistic effect of metal and carbon structures [1]. Engineering these hybrid materials and tuning their properties enabling them to find application in devices prove to be a challenging task. Hybrids of metal/carbon nanotube (CNT) composite structures can be synthesized by loading the metal particles over the carbon structures and vice versa. Recently, Bak et al. reported the synthesis of mesoporous nickel/CNT hybrids by electroless deposition technique to grow metal particles (nickel) over carbon nanotube substrate and Wang et al. developed a novel method for homogeneous dispersion of metal nanoparticles inside short CNTs [2,3]. CNT/nickel hybrid nanostructures were also synthesized by Jiang et al. and tested for pseudocapacitor application [4], similarly CNT-network modified Ni nanostructured arrays were synthesized by Zhu et al. for high performance non-enzymatic glucose sensors [5].

In addition to hybrids of metal/CNT composite structures, the hollow structure of CNTs was also exploited to produce nanotubes filled with a variety of metallic and non-metallic materials along the nanotube axis. Especially, ferromagnetic metal/carbon core/shell nanotubes (Fe, Co and Ni/CNTs) have been very attractive to researchers due to their size-dependent magnetic properties that are not observed in the bulk materials [6–10]. The CNTs encapsulated ferromagnetic materials have excellent thermal and chemical stabilities as they are well protected by the graphite layers against oxidation, which promote them as a potential candidate for application in harsh industrial environments where the stability of the nanostructures is crucial. During the past several years, a wide range of techniques have been developed for the synthesis of ferromagnetic metal/carbon core/shell nanotubes including chemical methods, electrolysis of molten salts, electrochemical deposition and chemical vapor deposition (CVD) [6,17–22]. Among these synthesis techniques, a significant development has been made by catalytic CVD (CCVD) for the mass production of ferromagnetic metal/carbon core/shell nanotubes and has led to potential applications. Generally, metallocenes and alloy catalysts were found to be very effective

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for the production of ferromagnetic metal/carbon core/shell nanotubes by CCVD [6,10,11,15,19,23–26]. Several mechanisms and approaches have been widely used to facilitate the growth of ferromagnetic metal/carbon core/shell nanotubes by CCVD [6,7]. The great potential applications of these ferromagnetic metal/carbon core/shell nanotubes are involved in various areas such as, high density magnetic recording media, magnetic resonance imaging, microwave absorption, sensors for magnetic force microscopy, electrochemical energy storage, drug delivery, biomedicines, and even for cancer treatment [11–16]. Among these avenues, the electrochemical energy storage in the nanostructure is quite interesting and a challenging task for material chemists. The storage of electrical energy will become increasingly important toward sustainable development. In recent years, rechargeable lithium-ion batteries have revolutionized portable electronic devices because of their superior energy density [27,28]. But in the present era of energy sustainability, whether to power the myriad consumer electronics or to improve the efficiency of hybrid electric vehicle and storage of wind/solar power, the need for energy storage will be vast. Current lithium-ion

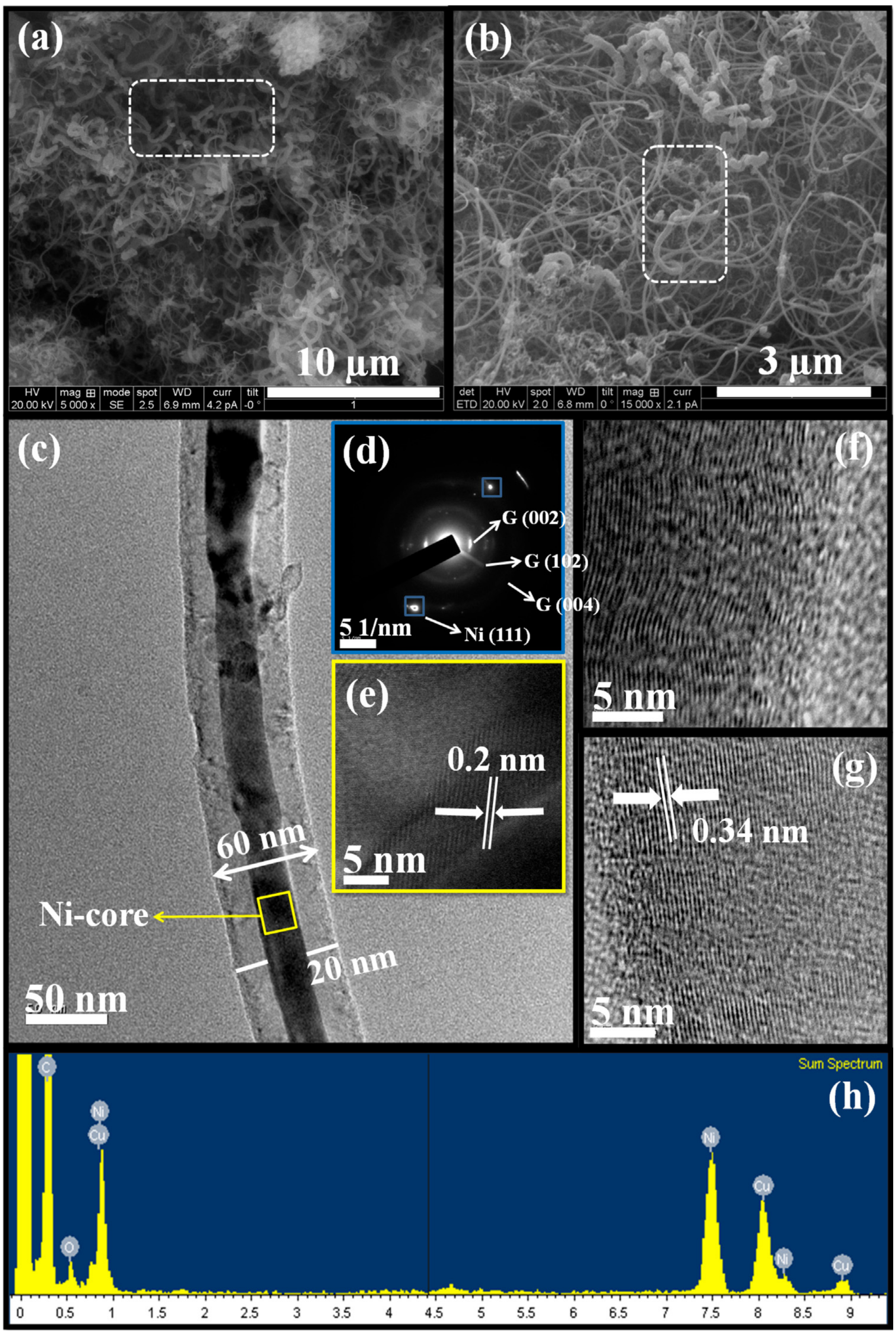

Fig. 1. (a, b) SEM images of Ni/CNTs core/shell structure at different magnifications, (c) TEM image of the Ni/CNT core/shell structure, (d) SAED pattern, (e) HRTEM image of Ni core taken from the square region, (f, g) HRTEM images of graphitic layers and (h) EDAX spectrum obtained from this fragment.