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Electrochemical growth of nickel nanoparticles on carbon nanotubes fibers: Kinetic modeling and implications for an easy to handle platform for gas sensing device

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ABSTRACT

An insight into the nucleation and growth mechanisms involved in the electrodeposition process of Ni nanoparticles is reported for macroscopic fibers consisting of aligned single wall carbon nanotubes (SWCNT). Electrochemical, micro-structural and Raman spectroscopy analyses have been utilized to investigate the electroactivity and the structure of the pristine and metal-decorated fibers. The study has pointed out the electrochemical properties of the bare fibers as electrode substrate and has highlighted the higher reactivity of these systems compared to conventional carbon microfibers toward metal electrodeposition phenomena.

Theoretical approaches previously developed for modeling metal electrocrystallization have been employed for describing the experimental current transients. The impact of non-random nucleation and anisotropic shape of nuclei on the kinetics has been taken into account by introducing a phenomenological parameter in the equation for the time-dependent current density.

It was found that an instantaneous nucleation process is responsible for a fast and efficient growth of Ni clusters on SWCNT fibers surface, which rules the formation of a hybrid metal-carbon nanostructures material with a high manageability and a potential wide field of application.

The pristine SWCNT fibers have proven to be an interesting platform for the assembly of an easy to handle gas sensor device. The present results show that the decoration with the nickel nanoparticles represents an efficient strategy to produce an active hybrid material with enhanced gas sensing properties.

1. Introduction

Carbon-based nanomaterials have attracted extensive attention from both the scientific and industrial communities since the discovery of C60, carbon nanofibers and carbon nanotubes in the 1980s. In recent times, a renewed interest is developing towards this eclectic class of nanomaterials thanks to the extraordinary discoveries made on graphene and detonation nanodiamond. However, large scale applications of nanocarbons are still limited, mainly because of the difficulty in their handling that causes a delay in the engineering of such intriguing materials. A possible efficient solution may be to combine C nanomaterials with each other or with other chemical species to form complex systems and/or hybrids that could actually be implemented in practical applications. In this field, many interesting researches have been undertaken in different laboratories around the world which analyze the synergistic effect between various C nanostructures assembled together, or between nanocarbons and organic/inorganic matrices combined in composite materials. The fields of application investigated for these systems are varied and range from electronics, energy storage and conversion, sensors up to biomedicine. Active materials for EMI shielding [1–3], actuators [4–6]; solar cells [7,8]; supercapacitors [9–11]; catalysis [12,13]; sensors [14–16]; drug carriers and scaffolds for tissue regeneration [17,18], and so on are just some examples of functional nanocarbons-based systems produced in recent years.

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In previous studies, we have been widely interested to integrate carbon nanostructures with other compounds. Great efforts have been done to optimize the processes of mixing different phases, aiming to control both the chemical functionality of the nanomaterials and the procedures for the preparation of composite materials. Thus, complex architectures based on hybrids of sp^2-sp^3 carbon [19–23] and Si structures have been successfully made using chemical vapor deposition techniques [24,25], while organic-inorganic composites have been obtained by chemical and/or electrochemical synthetic approaches [26–32]. In addition, great attention was given to the development of protocols for decoration of carbon nanotubes and nanodiamonds by metal nanoparticles. In particular, these studies allowed us to modulate both size and shape of the metal grains as well as the features of their coating in terms of particles density and coverage degree of the carbon phase, thus permitting to selectively produce hybrid systems with different chemical, optical and electrical properties [33–37].

Recently, we are focusing our attention on an interesting modality of SWCNT assembly, constituted by a self-standing and well-aligned macroscopic fiber produced by wet spinning of a SWCNT based liquid crystal [38]. Up to now, we have investigated the electronic properties of such an ordered nanotubes aggregate studying in detail the field emission process [39] and the effect of both potassium doping [40] and decoration by metal coatings [41] on the transport properties of the fibers. These studies have contributed to highlight the multiplicity of technological application of this ordered and easily processable carbon nanotubes system. The many studies conducted so far have basically shown the extraordinary mechanical, electrical, and thermal properties of these fibers that make them extremely competitive with respect to the more traditional polymeric and carbon fibers for uses ranging from high-value applications to consumer electronics [42]. However, a study aimed at determining the chemical reactivity of these systems has not yet been carried out. In particular, considering that the specific electrical conductivity of these fibers approaches that of metallic wires, an interesting analysis could be the evaluation of their electrochemical properties as electrode substrate. As it is well-known, the basis of an electrochemical event is the reaction at the electrode surface, which strongly influences the efficiency of an electrochemical reaction. Therefore, the knowledge of the surface properties becomes of fundamental importance for the development of innovative electrodes for batteries, supercapacitors, sensors, etc. based on these fascinating nanotubes systems.

On such basis, we found it stimulating to assess the performance of the SWCNT fibers with respect to the electrochemical phenomena typically involved into a metal electrodeposition process and make a comparison with what happens using conventional carbon microfibers. For this purpose, we carried out controlled reactions of Ni electrodeposition onto nanotubes fibers and industrial C microfibers by applying potentiostatic current-time transients. We investigated the mechanisms of nucleation and growth of the metal phase by describing the experimental results through a kinetic model. The morphology and structure of the obtained hybrid systems were then analyzed by means of electron microscopy and micro-Raman spectroscopy.

Finally, a study on the gas sensing properties was conducted for the first time on this typology of SWCNT fibers. It is well-known that carbon nanotubes have become one of the most popular sensing materials for gas detection due to their high sensitivity, fast response time, quick recovery time, and low operation temperatures. These features make carbon nanotubes (CNT) highly competitive if compared with metal oxide gas sensors. Actually, the unique structures and outstanding electronic properties of CNT make them an ideal candidate for the assembling of miniaturized and high-performance gas sensors and many studies have demonstrated the use of CNT-based systems in gas and chemical detection [43]. Surface modifications of CNT have also been proposed to promote the charge transfer between specific gas species and CNT. In particular, the decoration of CNT with metal nanoparticles to form hybrid systems is found to improve the CNT sensing performance, leading to enhanced sensitivity, faster response/recovery, and better selectivity [44–49]. In previous investigations, we carried out several studies related to gas detection by using resistive sensors assembled with SWCNT [50–53]. Therefore, taking advantage by the acquired experience in the field, in the present research we performed a preliminary study on the sensing properties of the bare SWCNT fibers and on the contribution of the Ni nanoparticles to the sensing performance of the Ni–SWCNT hybrid material towards NH_3.

2. Materials and methods

The SWCNT fibers were produced from concentrated dispersions of HiPco® single wall carbon nanotubes in 102% sulfuric acid via a high-throughput spinning technique [38]. Each fiber is characterized by a considerable nanotube alignment along its axe and possesses an external diameter of about 100 μm. The fibers are totally self-standing and exhibit lengths that can reach several centimeters.

The carbon microfibers were industrially produced from polyacrylonitrile (PAN) precursors and are assembled in 3000 filament count tows. The diameter of each filament is about 7 μm. Before use, they were subject to a cleaning treatment consisting of repeated washings in 2-propanol, HCl and acetone.

A conventional cell with a three-electrodes configuration was used for the electrochemical study. The SWCNT and C fibers were

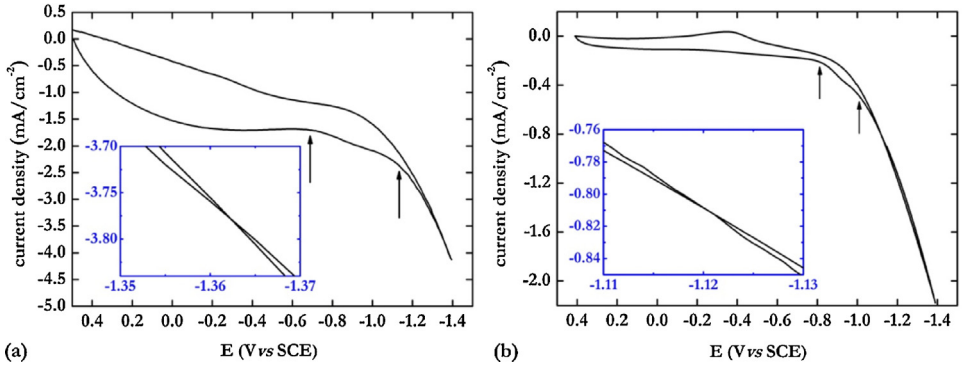

Fig. 1. CV curves referring to Ni electrodeposition onto (a) SWCNT fibers and (b) C microfibers; in the insets of both the images, the cross-over of currents is shown. The CVs were collected in Ni plating solution at 25 °C at a scan rate of 50 mV s^{-1}.