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Coatings based on conducting polymers and functionalized carbon nanotubes obtained by electropolymerization

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ABSTRACT

Nanocomposite films based on polyaniline, functionalized single-walled carbon nanotubes and different dopants were studied. These nanoporous composite films were grown electrochemically from aqueous solutions such that constituents were deposited simultaneously onto substrate electrode.

The synthetic, morphological and electrical properties of the obtained nanocomposite films were compared. Scanning electron microscopy (SEM) revealed that the composite films consisted of nanoporous networks of SWCNTS (single-walled carbon nanotubes) coated with polymeric film. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) demonstrated that these composite films had similar electrochemical response rates to pure polymeric films but a lower resistance and much improved mechanical integrity. The negatively charged functionalized carbon nanotubes (CNTSF) served as anionic dopant during the electropolymerization to synthesize polymer/CNTSF composite films. The specific electrochemical capacitance of the composite films is a significantly greater value than that for pure polymer films prepared similarly. Using these composite films, the modified electrodes with improved properties were obtained.

1. Introduction

Without carbon nanotubes, the thin conducting polymer films provide a high capacitance and reasonable response times, but they suffer from mechanical and chemical instability in life cycle tests, and low conductivity in the reduced or neutral states [1–8]. When the thickness of the polymer film increases, charge transport kinetics in the polymer becomes slow. These difficulties are all addressed by the addition of carbon nanotubes .For this reason, the researchers have sought to combine carbon nanotubes (CNTs) and conducting polymers (CPs) for use as modified electrodes in different promising applications including conductive and high-strength composites, energy storage devices, biosensors and various other devices.

Nanotubes themselves have provoked enormous interest over recent years, as a result of their unique properties and broad range of potential applications. Their very high mechanical resilience, high electrical conductivity and large surface areas are particularly relevant to their applications in supercapacitors. Carbon nanotubes (CNTs) and conductive polymers (CPs) are both interesting for their unique electrochemical properties. Many efforts have focused on the design and preparation of CNTs–CPs composites, in order to obtain a new material that would possess properties that would be useful in particular applications [1–18]. Composite materials based on the coupling of CPs and CNTs have been shown to possess properties of the individual components with a synergistic effect [1]. The CNTs doped CPs (conductive polymers) exhibit dramatically different electronic properties [2–8] compared to CPs prepared with small anionic dopants. Such differences reflect to conductivity of the CNTs dopant compared to the common insulating dopants. The electron flow within the CPs/CNTs is apparently increased by the entrapped CNTs due to an increased degree of delocalization and CNTs bridging [9,10]. In fact, impedance studies indicated that CPs/CNTs films are conducting even in their reduced state [9,10], i.e., a charge transfer occurs between the two constituents [7–15]. CNTs are however difficult to process and insoluble in most solvents. CNTs can be divided into two main categories: single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). The first is formed by a single graphene sheet. The latter are formed by additional graphene sheets wrapped around the SWCNT core. However, many of the potential applications of CNTs are hindered by the difficulties in their processing. The chemical functionalization of CNTs will play a key role in the realization of a material with much better properties. Thus, the solubilization of CNTs by attachment of long-chain molecules to the open ends of the nanotubes was the first step in bringing CNTs into the realm of molecular chemistry [16]. Rapid progress in development of

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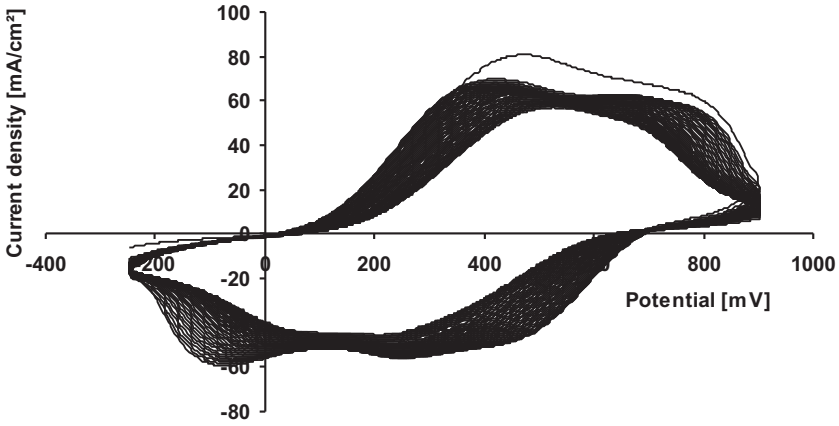

Fig. 1. Cyclic voltammograms of PANI/FSWCNTs composite film in 0.25 M H_2SO_4 cycling solution (monomer free) at 25 °C with a scan rate of 50 mV/s and for 50 cycles.

methods for covalent attachment of various organic groups [17–21], and biological molecules [22] has broadened the opportunities for applications of CNTs. With the advancement in the chemistry of CNTs it is now possible to tailor the electronic and chemical properties of CNTs [23,24]. Some of the important issues addressed by the chemistry of CNTs involve dissolution of CNTs and bundle exfoliation. The chemical functionalization of CNTs has been shown to increase their solubility in organic solvents and facilitate their processing [11,25,26]. It has also been demonstrated that the chemical functionalization affects the CNTs rope size and results in exfoliation into smaller bundles and individual nanotubes. These issues are especially important for the fabrication of high performance composite materials, controlled assembling of molecular electronics and development of ultra-high sensitive sensor devises. Here, we outline chemical approaches to functionalized single-walled carbon nanotubes (FSWCNTs) with an emphasis on their application for high-performance composites and biosensors.

In order to broaden their applications it was found necessary to tailor their solubility properties. For this reason, single-walled carbon nanotubes (SWCNTs) were covalent functionalized with a water soluble conducting polymer (carboxylic acids and octadecylamine which was noted thus – FSWCNTs). The FSWCNTs graft copolymer has excellent solubilities in water and some organic solvents and it also exhibits an order of magnitude increase electrical conductivity over neat simple polymer [18]. The presence of numerous functional groups in FSWCNTs means that there is potential for covalent immobilization of various biomolecules or dopants. Based on the above we expect composite materials based on the coupling of CPs and FSWCNTs to possess properties of each of the individual components with a synergistic effect.

In fact, composites of conducting polymers and carbon nanotubes have been synthesized by either chemical or electrochemical polymerization in the presence of carbon nanotubes (CNTs). In the chemical polymerization, an oxidant is needed but in this case the reduction product can affect the properties of the final product (nanocomposite). The reaction product is always a powder which means a binder has to be used for the construction of an electrode [27,28]. The binder is often an insulator and hydrophobic and hence, inevitably compromises the electrical and electrochemical performance. On the other hand, electrochemical polymerization has a number of advantages. Particularly, there is no need for added oxidants and electrodeposited conducting polymers are naturally integrated as a continuous uniform film on electrode, saving the use of a binder. Consequently, both the contact resistance within the polymer and between the polymer and the current collector are smaller than those of chemically prepared ones. Therefore, electrodeposited films are ideal for the study of the electrochemical properties of these composites and for practical uses, such as sensors, electrocatalysts and supercapacitors as discussed before [29–32].

In this paper is described electrochemical synthesis of nanocomposite films and electrochemical characterization of these nanocomposites by cyclic voltammetry, electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM).

2. Experimental

The electrochemical polymerizations were carried out using a conventional three electrodes system. A platinum electrode and a saturated calomel electrode (SCE) were used as counter and reference electrode, respectively. The reference electrode was placed in a separate cell and was connected to the electrolytic cell via a salt bridge that ends as a Luggin capillary in the electrolytic cell. This arrangement helps in reducing the ohmic resistance of the electrochemical system. The working electrode was made from a platinum disk with surface area of 0.5 cm^2. Functionalized single-walled carbon nanotubes (FSWCNTs) were provided by CarbonSolutions, Inc. (www.carbonsolution.com, Riverside, CA), and Aniline (99.5% Fluka) was used as supplied. Bidistilled water was used for all sample preparations. All chemicals were of the highest quality commercially available and were used as received.

Cyclic voltammetry and electrochemical impedance spectroscopy were used to investigate the electrochemical properties of the composite films. Electrochemical experiments were carried out with an automated model VoltaLab 40 potentiostat/galvanostat with EIS dynamic controlled by a personal computer. All the following potentials reported in this work are against the SCE (saturated calomel electrode). Scanning electron microscopy (SEM) was used to compare the microstructures of the deposited films.

2.1. Preparation of modified electrodes

The Pt electrode was carefully polished with aqueous slurries of fine alumina powder 0.05 μm on a polishing cloth until a mirror finish was obtained. After 20 min sonication, the electrodes were immersed in concentrated H_2SO_4, followed by thorough rinsing with water and ethanol. The prepared electrodes were dried and used for modification immediately. Nanocomposite films of CPs/FSWCNTs were prepared by electrochemical polymerization from a solution containing both the functionalized carbon nanotubes (FSWCNTs) and the corresponding monomer (aniline). Two kinds of FSWCNTs were used in this work namely: single wall carbon nanotubes (SWCNTs) functionalized with octadecylamine and single wall carbon nanotubes functionalized with carboxylic acids (see Schemes 1 and 2). In a first step, the FSWCNTs aqueous