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Electrochemical polymerization, optical and electrical characterizations of polycarbazole on single wall carbon nanotubes

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Abstract

Electrochemical polymerization of polycarbazole (PCz) on CVD grown, single wall carbon nanotubes (SWCNT), by using two-electrode cell is reported. This process was compared to cyclic voltammetry and three-electrode cell polymerization of PCz on bare conducting glass. The SWCNT were characterized by using Raman spectroscopy. Visible range transmission spectra of the PCz/SWCNT electrode exhibited spectroscopic characteristics similar to those of PCz on conducting glass electrode. On the other hand, differences were detected at the near IR spectral range. *I–V* measurements of the coated SWCNT films exhibited a general ohmic behavior and a substantial increase in the sample conductivity.

Keywords: Polycarbazole; Single wall carbon nanotube; Cyclic voltammetry; Electrochemical polymerization

1. Introduction

Fabrication of junctions between single wall carbon nanotubes (SWCNT) and electrically conducting polymers (ECP) has attracted much attention recently, in view of its potential applications in nanosize electronics [1–8]. In addition to the high surface area which may be exploited, SWCNT offer a unique quasi-one-dimensional structure that behaves either as a semiconductor or metallic conductor depending on the tube chirality [9,10]. At the same time, ECP portray tunable conductivity which depends on a redox reaction within the polymer chains and moreover, is sensitive to illumination of light [11,12] in some cases. Previous studies incorporated an ECP/SWCNT interface in numerous applications such as light emitting diodes [1,2], supercapacitors [3–5], printable conductors [6] and photovoltaic devices [7,8]. There are two approaches regarding the fabrication of the SWCNT/ECP electrode. In the first, the SWCNT and the ECP are mixed in solution followed by spin coating of a film on an appropriate substrate [1–3,6–8]. The other approach suggests that electrochemical polymerization is a more convenient and controllable way to coat the ECP on pre-deposited SWCNT [4,5,13]. Past research has demonstrated that it is possible to modify the polymer properties by parameter control of either the electrodeposition process or by the solution in which the polymerization process takes place. For example, one may modify the final product by varying the polymerization potential, the type of solvent used and the counter-ions [14,15]. This may enable the tailoring of the ECP/SWCNT junction properties for specific applications.

In the past, researchers investigated the electropolymerization of polyaniline and polypyrrole on SWCNT. Here we report for the first time on the electrochemical polymerization of polycarbazole (PCz). The studied ECP, polycarbazole (PCz) films have optical absorption in the ultra violet-visible range [16]. The SWCNT were grown on a substrate made of an ordered array of nanosize silica spheres (opal) and the electropolymerization of PCz on SWCNT occurred concurrently in this environment. Optical characterizations have been compared to electropolymerized PCz on flat, transparent, conducting glass electrodes. We used electrical

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measurements to characterize the samples as well. This is the first step towards fabrication of an optically controlled field effect transistor consisting of PCz/SWCNT junctions. Furthermore, recent non-linear optical experiments demonstrated the optical limiting effect of such composite films [17].

2. Experiments

The electrochemical experiments were conducted using three and two electrodes configurations. The three-electrode cell employed $Ag/AgNO_3$ as a reference electrode and platinum wire served as the counter electrode. All potentials were reported versus the $Ag/AgNO_3$ reference electrode. The working electrode was transparent conducting glass (Hartford Glass, 8 Ω/□ F-doped SnO_2 also known as, FTO) which was cleaned with water and soap, dipped for 10 min in solution consisting of analytical HF:H_2O (1:40 volume ratio) and then cleaned again with deionized water. A 273 EG&G Princeton Applied Research potentiosat–glvanostat was used to conduct the electropolymerization in this three-electrode cell. The two-electrode experiment was conducted using Oriel model 70705 power supply. The SWCNT imbedded silica nanospheres (Fig. 1a) were used as the anode electrode while stainless steel foil served as the cathode electrode. The polymer coated films are shown in Fig. 1b. Note the selective covering of polymer in areas with large concentration of SWCNT. A procedure published elsewhere was employed to prepare the ordered array of silica nanospheres [18]. In short, we formed silica nanospheres by hydrolysis of tetraethoxysilane in a mixture of ammonium hydroxide, water and ethanol. The dispersion of nanospheres in ethanol was followed by the addition of a methanol solution containing cobalt nitrate. The resulting suspension was let dried and the resultant opaline structure was self-assembled on quartz substrates. The SWCNT were grown by chemical vapor deposition (CVD). The opaline substrate was placed inside a quartz reaction tube located in the middle of a horizontal tubular furnace. The growth of the SWCNT was preformed according to the following procedure: 30 min in air at 500 °C to decompose the cobalt nitrate to the corresponding oxide, 30 min in pure hydrogen at 500 °C to convert the oxide to sub-oxide and metal particles. The reaction zone temperature was then raised to 700 °C, and subsequently pure CO was introduced at 700 °C and 1 atm at a flow rate of 100 cm^3/min and kept under these conditions for 30 min. After completion of the reaction, the reactor was allowed to cool down under flowing argon. The individual and small bundled SWCNT (a typical TEM picture is provided in [18]) formed a continuous, three-dimensional electrical network via tube-tube interaction. This continuity created a macro-electrode suitable for electrochemical deposition of PCz. The characteristics of the electrode made of SWCNT were analyzed using Raman spectroscopy (Fig. 2). After

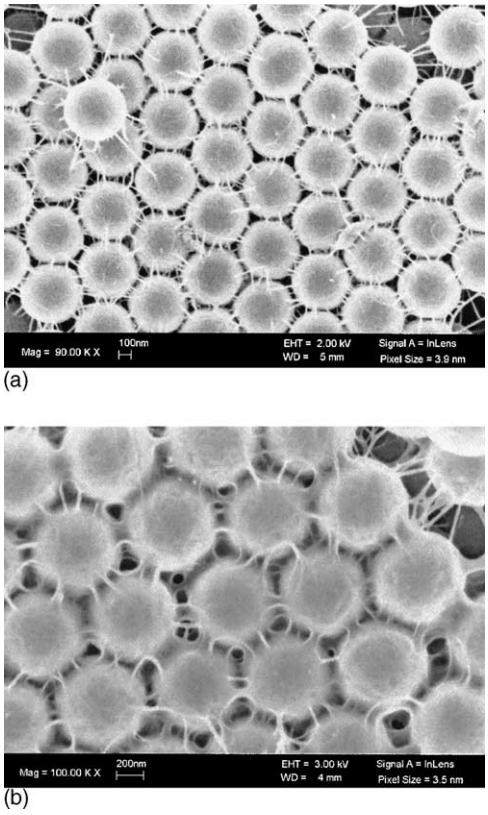

Fig. 1. (a) SWCNT grown within the voids of opaline structure; (b) PCz/SWCNT film. Note the selective covering areas of the polymer.

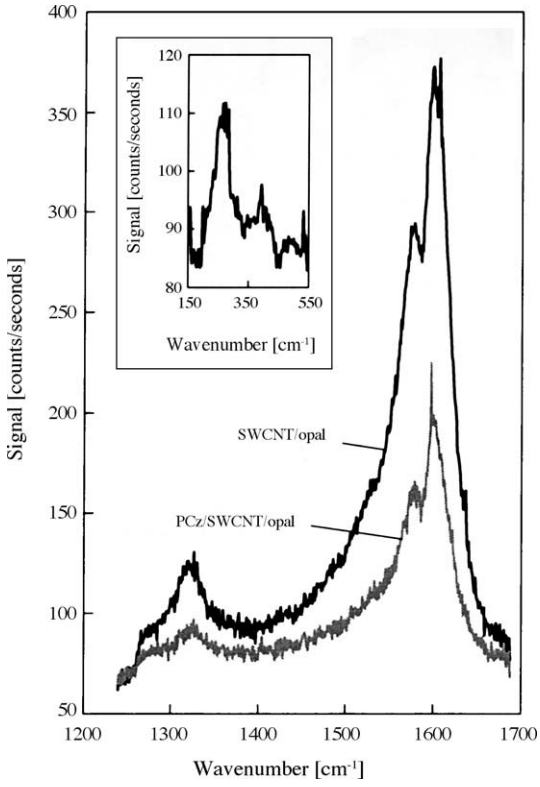

Fig. 2. Raman spectra of SWCNT in opalline structure. The inset shows the low frequency of only the SWCNT/opal electrode. The signal for the PCz/SWCNT was similar yet, weaker.