Aligned Coaxial Nanowires of Carbon Nanotubes Partially Sheathed with Polyaniline for Chemical Sensors

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The aligned carbon nanotube–polyaniline composites with partially coaxial structures were prepared by electrochemical polymerization of aniline, which show efficient electrical conduction attributed to the polyaniline layer and large surface or interface area for potential application in chemical sensors.

Since the discovery of carbon nanotubes (CNTs) by Iijima,[1] the investigation of composite materials with CNTs has attracted enormous interest both in scientific and technological fields because of their unique thermal, metallic, electronic, and mechanical properties and a wide range of promising applications in nanoelectronics devices, biological devices, and high strength polymer composites.[2] The use of aligned CNTs provides additional advantages in electron-emitting displays, advanced biosensors, and electromechanical actuators for maximized access of the nanotube surface and efficient device construction.[3]

Conducting polymers (CPs) have emerged as most potential commercial materials owing to their interesting optical and electronic properties.[4] Because of the large band energy (>3 eV), CPs need a doping process to bring them to a conductive state. This doping process is in a chemically or electrochemically reversible manner and thereby promotes simultaneous changes in volume, color, electrical conductivity, and other properties.[5] Among these conductive polymers, polyaniline has been investigated for various applications over the past decades.[6] In recent years, one-dimensional polyaniline materials with nanostructures, including nanowires, rods, and tubes, have received considerable attention as promising candidates for fabricating smart devices, and such materials will possess the advantages of both low-dimensional systems and organic conductors.[7]

To achieve a synergistic effect, the combination of CNTs and CPs has been demonstrated to lead to high-performance composite materials for optoelectronic devices.[8] In this regard, we report a novel concept of combination of CNTs and polyaniline polymer for fabricating chemical sensors. Figure 1 describes the detailed procedures of fabricating aligned carbon nanotubes (CNTs)–polyaniline (PANI) composites for a chemical sensor. The nanowires of aligned CNT array partially sheathed with PANI possess much faster gas-phase doping/dedoping times compared with conventional electrochemical polymerized PANI films, which indicates promise for sensor applications.

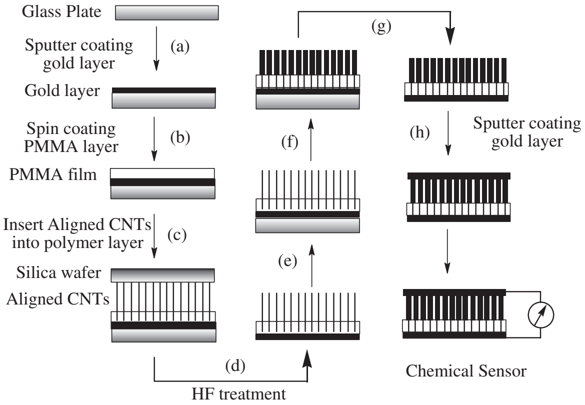

Figure 1. Schematic illustration of the procedures for fabricating the aligned carbon nanotubes (CNTs)–polyaniline (PANI) composites chemical sensor.

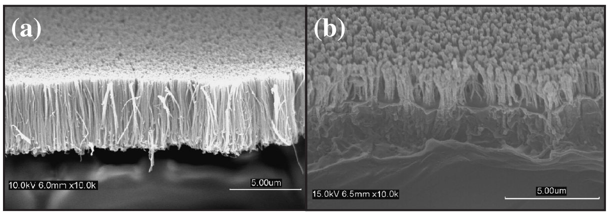

Figure 2. SEM images of (a) the as-prepared aligned carbon nanotube array, (b) the aligned carbon nanotube array half embeded into PMMA film after electrochemical polymerization of aniline.

The aligned multiwalled carbon nanotubes were prepared by pyrolysis of iron(II) phthalocyanine (FePc) within an Ar/H_2 flow at 800–1100 °C, according to a method reported previously.[9] Figure 2a depicts a typical scanning electron microscopic image of the resultant carbon nanotube arrays. The as-prepared nanotubes are well graphitized with ca. 40 layers of graphite sheets, a length of ca. 5 µm and an outer diameter of ca. 50 nm.[10] First of all, a thin layer of poly(methyl methacrylate) (PMMA) was spin-coated onto a flat glass substrate with a thin layer of sputtered gold film from a 40 wt % chloroform solution at a rate of 600 rpm for 2 min (Figures 1a and 1b). The thickness of PMMA layer was about 2.5 µm in constituent condition (Figure S2), and it can be well controlled by spin-coating rate and solution concentration.[12] After that, the substrate was heated at a temperature (150 °C) above the glass-transition temperature (about 105 °C) of PMMA, and then the aligned carbon nanotube carpet was inserted into the polymer layer vertically (Figure 1c). When the temperature of glass substrate was cooled to room temperature, the composite was dipped into HF solution (30% w/w) to remove the silica wafer (with a thin layer of SiO_2 on the surface and used as the substrate for growing aligned CNTs) and glass substrate (Figure 1d).[11] As shown in the SEM image in Figure 2b, the aligned CNTs were successfully transferred and anchored into the PMMA layer with a protruding section of about 2 µm. This indicated that the other side of the aligned CNT carpet contacted directly with the gold layer. Thus, the aligned conducting CNTs can be used as the microelectrodes to make novel conducting polymer–carbon nanotube coaxial nanowires by depositing electrochemically a concentric layer of conducting polyaniline uniformly onto each of the partially protected aligned CNT with PMMA layer.[8b]

In a typical experiment, the aligned CNT carpet with partial section embedding into PMMA layer was attached on another clean glass substrate, and the edge of gold layer was sealed with PMMA film to avoid electropolymerization of aniline occurring on the opposite surface of the gold layer (Figure 1e). Subsequently, a cyclic voltammetric method was employed to deposit a concentric layer of polyaniline, using the aligned CNTs in contact with the gold layer, platinum plate and Ag/AgCl as work, counter, and reference electrodes, respectively (Figure 1f). As shown in Figure S1, aniline oxidation peak at about 1.14 V was observed in the first cycle.[12] With increasing cycle times, two new peaks at 0.3 and 0.8 V, attributed to the oxidation of polyaniline appeared and became stronger, indicating the continuous formation of polyaniline layer. After the electropolymerization, the color of the nanocarpet surface became green, which gave the direct proof that polyaniline emeraldine base film had deposited on the CNT electrodes. The evidence of formation of the uniform polyaniline layer on CNT array was also supported by the SEM image (Figure 2b). The size of the diameter of polyaniline wire is much larger than that of the pristine CNTs, which also support the formation of polyaniline layer on the surface of CNTs. Figure S3 shows the surface morphology of the aligned CNTs covered with the concentric layer of polyaniline. A discrete surface was observed after six cycles of electrochemical polymerization (Figure S2a).[12] When the cycle times increased to fifty, the discrete surface became continuous, which indicated that the PANI polymer had fully filled the gaps of the constituent aligned CNT array (Figure S3b).[12] These partically coaxial structures are expected to provide efficient electrical conduction to and from the PANI layer and large surface or interface area for application in chemical sensors (Figure 1).

For comparation, we measured at the same time the sensor properties of the PANI–CNT coaxial nanowires with discrete and continuous surfaces, the pristine partical embedding CNTs (the aligned carbon nanotube array with partial embedding into PMMA film before electrochemical polymerization of aniline) and pristine PANI film (electrochemical deposition of polyaniline directly onto gold film for six cycle times without CNTs). Figure 3 shows the real-time resistance changes (R/R_0) of dedoped films monitored with an electrometer (Keithley Model 6485 picoammeter), upon exposure to 100 ppm of HCl (Figure 3a), and the same fully HCl-doped films exposed to 100 ppm of NH_3 (Figure 3b). This process can be carried out for more than 100 times implying the good reversibility. The PANI–CNT coaxial nanowires with discrete surface responds much faster than the nanocarpet film with continuous surface and pristine PANI film to both acid doping and base dedoping. This is due to the small diameter of PANI–CNT coaxial nanowires that afford a high surface area within the film that can be accessed by the gas vapor. On the other hand, the discrete surface also gives rise to a porosity of the nanocarpet film, which enables gas molecules to diffuse in and out of the sensor film easily and quickly. After the gap of each constituent aligned CNT fills with PANI, the surface area becomes smaller and loses the nonporous nature, which will take a long time for much great extent of doping or dedoping process. The response time finally can be compared with the pristine PANI film without nanotube electrodes.

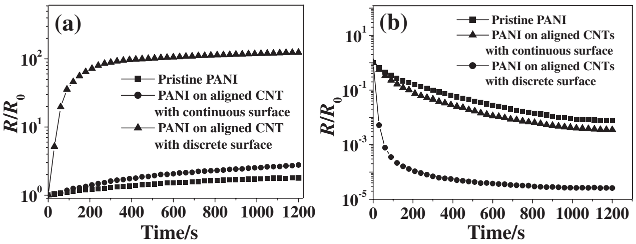

Figure 3. Real-time resistance changes (R/R_0) of dedoped films (a) upon exposure to 100 ppm of HCl, and (b) the same fully HCl-doped films exposed to 100 ppm of NH_3.

In summary, we developed a new concept of combination of CNTs and polyaniline polymer for fabricating chemical sensors. These partially coaxial structures were prepared by electrochemical polymerization of aniline using the partially protected aligned CNTs by PMMA layer as the microelectrodes. The devices are expected to provide efficient electrical conduction to and from PANI layer and large surface or interface area for potential application in chemical sensors.

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