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Single-wall carbon nanotube chemical attachment at platinum electrodes

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ABSTRACT

Self-assembled monolayer (SAM) techniques were used to adsorb 4-aminothiophenol (4-ATP) on platinum electrodes in order to obtain an amino-terminated SAM as the base for the chemical attachment of single-wall carbon nanotubes (SWCNTs). A physico-chemical, morphological and electrochemical characterizations of SWCNTs attached onto the modified Pt electrodes was done by using reflection-absorption infrared spectroscopy (RAIR), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, scanning electron microscopy (SEM), atomic force microscopy (AFM), and cyclic voltammetry (CV) techniques. The SWNTs/4-ATP/Pt surface had regions of small, medium, and large thickness of carbon nanotubes with heights of 100–200 nm, 700 nm to 1.5 μm, and 1.0–3.0 μm, respectively. Cyclic voltammetries (CVs) in sulfuric acid demonstrated that attachment of SWNTs on 4-ATP/Pt is markedly stable, even after 30 potential cycles. CV in ruthenium hexamine was similar to bare Pt electrodes, suggesting that SWNTs assembly is similar to a closely packed microelectrode array.

1. Introduction

Since the discovery of carbon nanotubes by Iijima [1], a spurt of research activities have been focused on single-wall carbon nanotubes (SWCNTs). SWCNTs exhibit an interesting combination of remarkable physico-chemical properties such as their dimensions (high length-to-diameter ratio), strength, chemical stability, as well as mechanical and electronic properties. These properties make them attractive and suitable for several areas of potential applications such as biomolecular recognition [2], reinforcement in polymer composites [3,4], scanning probe microscopy tips [5,6], chemically sensitive imaging of materials [7], transistors and logic circuit construction [8,9], hydrogen storage [10,11], support for metal catalysts [12] and lithium intercalation [13]. Most of these applications require molecular devices with a 3D nanostructure of monodispersed and aligned nanotubes [10]. The fabrication of many nanoelectronics devices frequently includes carbon nanotubes as a fundamental constituent [14–17].

Understanding the chemistry of carbon nanotubes is essential in order to explore their ultimate potentialities for practical uses. The exposed surface of carbon nanotubes is made up of unreactive basal graphitic plane, and hence at the first sight, they may appear to be chemically inert; however, when treated with acids their surfaces can be highly functionalized. SWCNTs are generally produced by the conversion of the sp^2-hybridized carbon into its sp^3 form. Oxidation studies show that carbon nanotube ends are etched away via chemical oxidation, resulting in open-ended tubes [18]. Oxidized carbon nanotubes have several oxygen-containing functional groups such as phenol, carbonyl, carboxyl, at their open ends and side-wall defect sites, which make them more reactive than pristine SWCNTs. Consequently, smaller fragments of SWCNTs obtained by acid treatment are important intermediates for the fabrication of SWCNTs devices. Individual SWCNTs deposition on chemically functionalized surfaces is a method that facilitates the formation of nanostructure devices from carbon nanotubes. The carboxyl functionalized ends of SWCNTs enable the attachment of carbon nanotubes to an amino-terminated self-assembled monolayer (SAM) deposited over a metal surface.

The ideal acylating reagent would be a carboxylic acid, but the acids themselves are relatively unreactive with nucleophiles. A possible route to make them active is to convert the carboxylic acid to a more reactive derivative such as an acyl chloride or anhydride. Yet another route would be to employ reagents that selectively activate a carboxyl group toward nucleophilic substitution. Two such reagents are dicyclohexylcarbodiimide (DCC) and carbonyldiimidazole (Staab's reagent) [19,20]. One of the most common methods for formation of an amide bond is the activation of the acid with carbodiimides, particularly, DCC, and its subsequent reaction with an amine (see Scheme 1).

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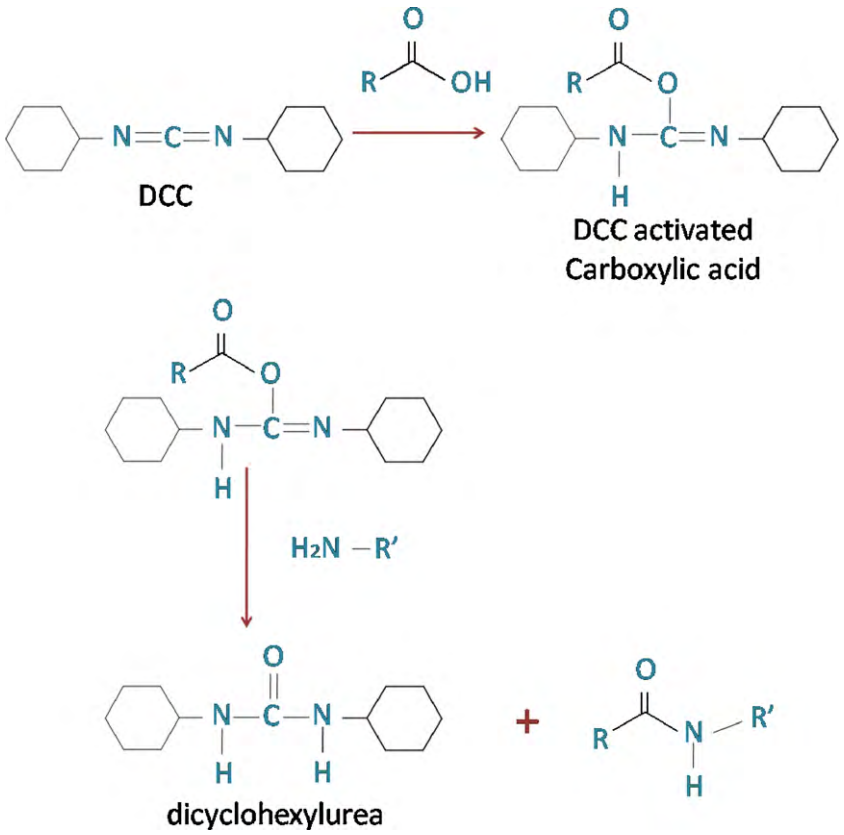

Scheme 1. A general scheme for the reaction of dicyclohexylcarbodiimide (DCC) activating carboxylic acid toward amide formation.

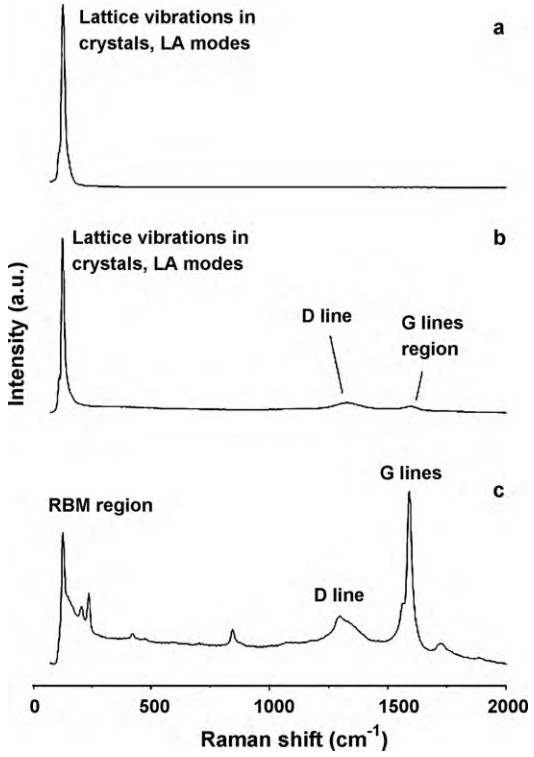

Fig. 1. Raman spectra of (a) an unmodified, (b) ethanol/SWCNTs treated, and (c) 4-ATP/SWCNT modified Pt electrode.

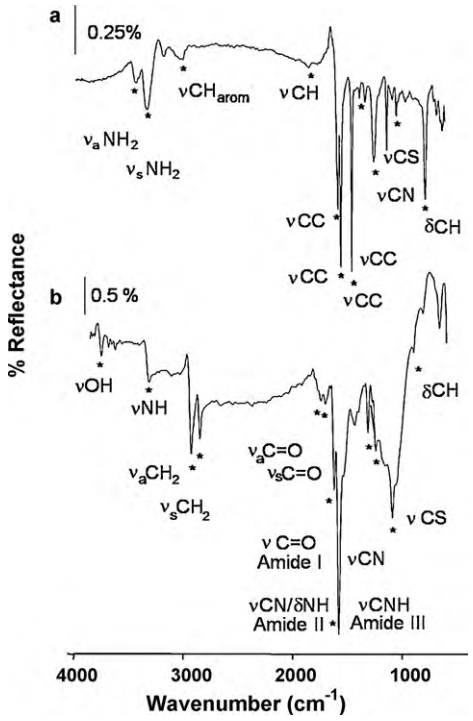

Fig. 2. Reflection-absorption infrared spectra of the (a) 4-ATP and (b) 4-ATP/SWCNTs/modified Pt electrodes.