Mercury(II) Immobilized on Carbon Nanotubes: Synthesis, Characterization, and Redox Properties

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Mercury(II)-modified carbon nanotubes can be readily prepared by reacting purified/oxidized carbon nanotubes (CNTs) with a Hg(NO\textsubscript{3})\textsubscript{2} aqueous solution. Two types of surface-confined Hg(II) species are formed and have been identified as (CNT-COO\textsubscript{-})Hg\textsuperscript{II} and (CNT-O\textsubscript{2}H)Hg\textsuperscript{II}. These two complexes have a surface concentration ratio of about 30:70%, on the basis of data obtained from high-resolution XPS spectra, Raman spectroscopy, and electrochemical measurements. The electrochemical behavior of Hg(II)-modified CNTs adhered to electrode surfaces in contact with CH\textsubscript{3}CN (electrolyte) strongly depends on the nature of the working electrode used and the size of electrolyte cation. Significant voltammetric changes also are observed after the addition of water to the initially water-free acetonitrile electrolyte solution. At a glassy carbon electrode and using NaClO\textsubscript{4} as the electrolyte, a proposed mechanism is operative. However, at a gold-coated quartz-crystal electrode, Hg formed after reduction reacts with the Au to form Hg–Au alloy which has a very positive stripping peak potential value compared to that for the Hg film formed on glassy carbon surfaces. The influence of the electrolyte cation size on the reduction of Hg(II)-modified CNTs is attributed to the intercalation of electrolyte cations.

Introduction

There has been intense interest in carbon nanotubes (CNTs) since their discovery by Iijima in 1991\textsuperscript{1} mainly because of their structural, electronic, and mechanical properties.\textsuperscript{2} CNTs are fullerene-related structures which consist of one or several graphene cylinders closed at either end with caps containing pentagonal rings.\textsuperscript{3} They have proved to be promising candidates in a wide range of applications including, for example, the storage of hydrogen and other gases,\textsuperscript{4,5} quantum wires,\textsuperscript{6} electronic devices,\textsuperscript{7} ultra high-strength engineering fibers,\textsuperscript{8,9} and catalyst supports.\textsuperscript{10–12} Opening/oxidation and subsequent filling/coating of CNTs with foreign materials such as metals,\textsuperscript{14} metal oxides,\textsuperscript{15} proteins\textsuperscript{16–18} and enzymes\textsuperscript{19} are anticipated to be very important steps toward their practical applications both in material and in biological sciences. Recently, electrochemical studies on dopamine\textsuperscript{19,20} and proteins\textsuperscript{19,20} using CNTs as a component in a composite carbon-nanotube paste electrode were reported. It was concluded that the electrochemical response of dopamine at a nanotube electrode is significantly superior to that observed at other carbon electrodes.\textsuperscript{20} Despite the fact that a large number of different types of materials have been inserted/deposited into/on CNTs, only in a few cases have the electrochemical studies on these modified CNTs been reported, probably because conventional solution-phase and solution-casting “film” methods are not suitable.

In this paper, Hg(II) ions are grafted on the surface of oxidized CNTs and the electrochemistry of the Hg(II)-modified CNTs, which is referred to as Hg\textsuperscript{II}NT thereafter, are reported in CH\textsubscript{3}CN (0.10 mol L\textsuperscript{-1} NaClO\textsubscript{4}). Ground Hg\textsuperscript{II}NT powders were mechanically attached to electrode surfaces, and only a very small amount of Hg I\textsubscript{INT} (<15 mg of purified CNTs) was required to undertake the electrochemical studies reported herein.

Experimental Section

(a) Chemicals. Raw CNTs was purchased from Strem Chemicals (Newburyport, MA), which contains 40–50% multiwalled CNTs with the remainder being other forms of carbons (see Results and Discussion section for details). Acetonitrile (HPLC grade, Mallinkrodt) was dried over 3 Å activated molecular sieves and passed twice through a column (about 40 cm long) packed with alumina that had been dried at 400 °C overnight. NaClO\textsubscript{4} (Ajax, Auburn, NSW, Australia) was of analytical purity grade and dried at 100 °C under N\textsubscript{2} for 12 h prior to use. All other chemicals used were of analytical grade purity.

(b) Purification/Oxidation of CNTs. Many oxidants, such as HNO\textsubscript{3}, H\textsubscript{2}SO\textsubscript{4}, Br\textsubscript{2}, O\textsubscript{3}O\textsubscript{4} and RuO\textsubscript{4}, have been employed to

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