The modification of carbon nanotubes in the Nafion matrix on the surface of glassy carbon electrode and its application as electrochemical sensor

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Carbon nanotube, a type of graphitic tubular material of nanometer size, has attracted intensive interest since its discovery in 1991 [1], due to its widely believed potential application as one-dimensional quantum material [2]. Theoretical calculations predicted that this material could behave either as a metal or a semiconductor depending on its size and lattice helicity. The body of nanotubes, either multi-walled or single walled, can be considered as the curved graphite layer(s) with the typical hexagon carbon arrangement, while the tips of the nanotubes are cap-like structures consisting both pentagon and hexagon carbon rings. The chemical reactivity on a nanotube has been related to the strain energy stored by the curved structure (on both tube’s body and tips) and the strained pentagon structure (only on tips). The chemical reactivity of nanotubes in solution have been demonstrated, resulting in specific reactive (oxidative) sites on the nanotube’s surface.

The subtle change of structural and electronic properties of carbon nanotube with respect to that of graphite suggest that carbon nanotube has a higher chemical reactivity in addition to the ability to mediate electron transfer reactions in solution when used as an electrode. Our group [3] have recently reported that nanotube electrode was prepared by gently pressing nanotubes into a capillary and is immersed in a concentrated perchloric acid. Apparent irreversible oxidation of carbon nanotubes was observed at +1.10 V vs. Ag/AgCl by high resolution transmission electron microscopy and by Raman spectroscopy. We suggested that the layer dislocation (organisation defect) in the architecture of the multi-walled nanotube being a major source of reactivity on both the tip and the body of the carbon nanotubes. Most interestingly, the carbon nanotube’s tip can be opened up by electrochemical oxidation, presumably due to the higher chemical reactivity at the tip, compared with that on tube’s body.

In this study, the modification of carbon nanotubes in the Nafion matrix is achieved on the surface of a glassy carbon electrode (GCE). The nanotube electrode shows a marked enhancement of the current response and a 400 mV potential shift for the reduction of dissolved oxygen (DO) when compared with that of the bare GCE. Neither the diffusion of the reactant nor the surface reactions controlled the reduction process of DO. The electrochemical activation of the nanotube electrode was studied in acidic, neutral and basic solution at different potentials by selecting uric acid as a model compound. A better effect is achieved when the nanotube electrode is activated in perchloric acid. The adsorptive accumulation of uric acid at the surface of nanotubes is combined with the subtle electronic properties of nanotubes to reach a detection limit of 6.0×10⁻³ M (S/d = 3). The practical analytical application of this carbon-nanotube modified electrode is

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demonstrated by the measurement of uric acid in human urine in a selective, sensitive and quantitative manner without any preliminary treatment of the sample.

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Fig. 1 Differential pulse stripping voltamograms of the title electrode in a solution containing (a) 0, (b) 3.0x10^{-7}, (c) 6.0x10^{-7}, (d) 1.2x10^{-6}, (e) 2.5x10^{-6} and (f) 5.0x10^{-6} M uric acid, respectively. DPSV parameters: rotation rate, 400 r.m.p; deposit time, 480 sec; pulse amplitude, 50 mV; pulse width, 50 msec; pulse period, 200 msec; scan rate, 20 mV.s^{-1}; sample width, 10 msec.