The 2011 H. H. Uhlig Summer Research Fellowship — Summary Report Catechol-encapsulated Multi-walled Carbon Nanotube Modified Electrode as a New Generation Electrocatalyst for NADH Oxidation

by Puchakayala Swetha

Since 1984, several attempts have been made to stabilize the biochemical mediator, catechol (CA) as a surface confined electrode and further to utilize it as an electro-catalyst for NADH oxidation¹. Unfortunately, electrode preparation involves tedious synthetic steps and the electrodes are unstable.² In our recent preliminary communication, we have found a new electrochemical preparation for the CA-encapsulated multi-walled carbon nanotube (MWCNT) modified glassy

carbon electrode designated as GCE/CA@ MWCNT³ by potential cycling of GCE/ MWCNT in 1mM of CA dissolved neutral pH. The electrode shows stable and welldefined redox behaviors at an E° values of 0 (A1/C1) and 0.2 V (A2/C2) vs Ag/AgCl, due to the surface confined chemisorbed and diffusion controlled physisorbed CA species respectively (Fig. 1a, curve a).³ In this work we are exploiting the CA@MWCNT modified electrode for NADH oxidation for the first time. As shown in curve b of Fig. 1a, in the presence of 1 mM of NADH, the GCE/CA@ MWCNT shows a profound oxidation signal where the surface confined A1/C1 redox peak appeared. A control experiment with CA unmodified electrode, GCE/MWCNT yielded a 20 times decrease in the NADH current signal along with 200 mV increase in the oxidation potential (i.e., 200 mV of

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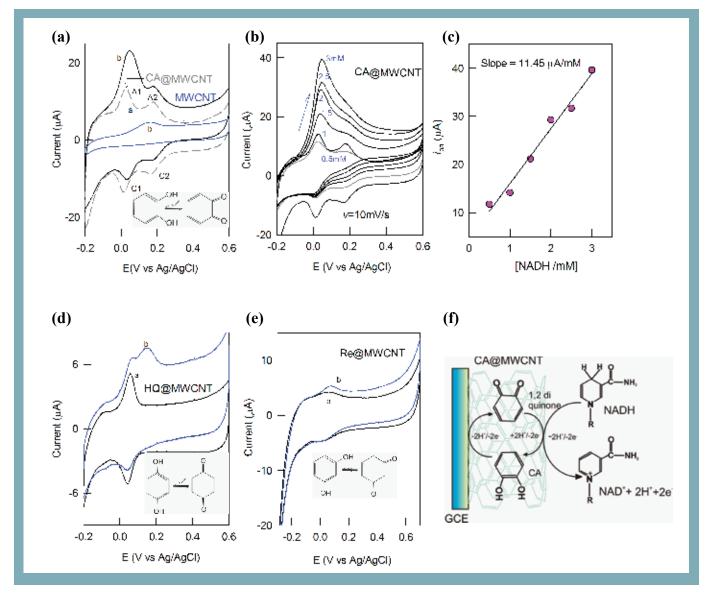


FIG. 1 (a) CV of NADH electrocatalytic oxidation (a = without and b = with 1mM NADH) at GCE/CA@MWCNT and GCE/MWCNT electrodes. (b) Effect of concentration of NADH (0.5mM-3mM) a GCE/CA@MWCNT. (c) Linear calibration plot of NADH concentration (mM) vs current (i_{pa}) at v = 10 mV/s. (d, e) NADH electrocatalysis at GCE/HQ@MWCNT and GCE/Re@MWCNT. (f) Illustration of the CA@MWCNT and its NADH electrocatalysis.

over-potential). A possible mechanism for the electrocatalysis is the electro-generated 1,2 diquione can chemically oxidize NADH to corresponding NAD⁺ which in turn forms CA as reduced redox species. The calibration plot was linear up to 3 mM with a current sensitivity of 11.45 μ A/mM.

We have also tested NADH oxidation on different isomers of CA, hydroquinone (HQ) and Resorcinol (Re) immobilized MWCNTs, i.e., HQ@MWCNT and Re@ MWCNT (which are prepared similar to the CA@MWCNT³). Among the systems, the HQ@MWCNT shows some NADH oxidation current signal, which is relatively weak when compared with CA@MWCNT; while the Re@MWCNT failed to show any electrocatalysis. The absence of electrocatalysis with Re@MWCNT may be due to the formation of a non-conjugated 1,3-diquinone intermediate, which may be less stable and non-reactive, characteristic inside the CNT matrix. In conclusion, the GCE/CA@MWCNT is efficient for electrocatalytic NADH oxidation and extendable for various NADH coupled biosensing systems.

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