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Investigation of the Mechanism of Adsorption of β-Nicotinamide Adenine Dinucleotide on Single-Walled Carbon Nanotubes

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ABSTRACT We address in this manuscript the important issue of the stability of single-walled carbon nanotube (SWCNT)-based electrodes upon oxidation of NADH to NAD^+. NADH and NAD^+ play a key role in the development of electrochemical enzyme-based biofuel cells and biosensors. However, most of the electrode materials exhibit strong surface passivation when oxidation of NADH to NAD^+ occurs. SWCNT-based electrodes are not affected by such a passivation effect. In the present work, we address the fundamental question, "why are the single-walled carbon nanotube electrodes prone to passivation?" using electrochemical methods and first-principles molecular dynamics simulations. We found that this is due to the wide exposed surface of SWCNT-based electrodes rather than other "inherent" properties of SWCNTs, such as the electrocatalytic effect and high curvature.

SECTION Molecular Structure, Quantum Chemistry, General Theory
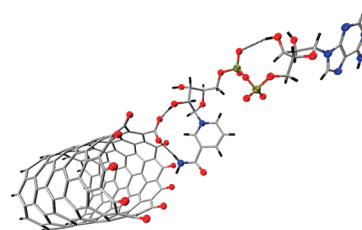
NADH and NAD^+ are key systems in electrochemical enzyme-based biofuel cells and biosensors.[1−8] However, most of the electrode materials, such as metals or carbon-based electrodes (glassy carbon, highly oriented pyrolytic graphite), exhibit strong surface passivation upon oxidation of NADH to NAD^+.[1] Such electrode passivation has a drastic undesirable effect upon the reproducibility and stability of NADH/NAD^+-based biosensors and energy storage systems.[9] Carbon-nanotube-based electrodes exhibit exceptional resistance to the passivation effects.[10−12] Most of the studies on the stability of carbon nanotubes toward NADH passivation are conducted on multiwalled carbon nanotubes (MWCNTs), and typically, only electrochemical methods are used as experimental probes. We report here a systematic investigation of the reasons for the stability of a single-walled carbon nanotube (SWCNT) electrode and adsorption of NAD^+ on CNTs by means of voltammetry, amperometry, and Car−Parrinello molecular dynamics (CPMD) simulations[13,14] within Becke and Lee−Yang−Parr gradient corrections on the exchange and correlation functionals.[15,16] This computational approach has been already applied with success to similar problems.[17,18] Our target systems, SWCNTs, have been selected because they allow for a direct comparison with experiments.

First, we performed voltammetric and amperometric measurements to study the adsorption of NAD^+ experimentally.

Figure 1A shows amperometric response to the oxidation of 5 mM NADH at a SWCNT-based electrode in the stirred solution. The electrode displays a very minor decrease of current, from 56.9 to 51.2 μA (−10%), and proves high stability of the electrode toward passivation. In addition, the electrochemical oxidation of NADH on SWCNTs recorded in voltammetric experiments before (Figure 1B, a) and after (Figure 1B, b) being left in the 5 mM NADH solution for 60 min at an applied potential of +0.9 V takes place at 740 and 810 mV, respectively, with oxidation peak currents of 17.5 and 16.4 μA, respectively. Apparently, the oxidation wave shifts slightly to positive values, which is a sign of electrode passivation. However, such a shift is very small, and the difference in magnitude of current is negligible; thus, the magnitude of electrode passivation is very small. These results compare well with previous observation using MWCNTs.[1,10−12] There are two possible explanations of such observations; (i) the interaction of NADH/NAD^+ with CNTs is fundamentally different from the interaction with planar graphene sheets of graphitic electrodes, or (ii) the high surface area of CNT electrodes is not affected by the passivation of
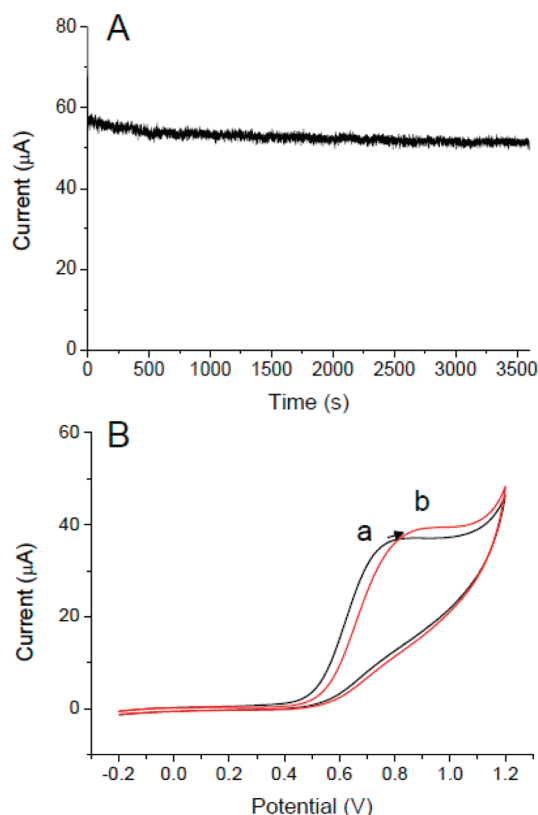
Figure 1. (A) Chronoamperometric response of a SWCNT-modified electrode to 5 mM NADH as recorded for 60 min. Conditions: phosphate buffer, 50 mM, pH 7.4, stirred solution, 400 rpm, applied potential, +0.9 V. (B) Voltammetric responses of NADH on a SWCNT-modified electrode (a) before and (b) after being left in a 5 mM NADH solution for 60 min under an applied potential of +0.9 V.

NADH **placed on the SWCNT (10,0)** $\Delta E \leq 0.1$ eV

NAD$^+$ **placed on the SWCNT (10,0)** $\Delta E \leq 0.1$ eV

Figure 2. Geometry of the NADH positioned on top of the nanotube (10,0) after 5 ps of molecular dynamics (MD) simulation (top). Geometry of NAD$^+$ positioned on the top of the nanotube (10,0) after 5 ps of MD (bottom).

NADH/NAD$^+$ on the electrodes, even though such adsorption occurs.

To give an atomic-level insight to address this issue, we performed CMPD simulations. These simulations were focused on the interaction of NADH and NAD$^+$ with a SWCNT along its exposed surface and at the edge. For the case of the NAD$^+$ positioned close to the edge, in order to reduce the computational workload, we modeled the system with a portion of the nonmetallic carbon nanotube (10,0) (3 unit cells) saturated at one end with H atoms; the other end was saturated with different chemical species in order to investigate the effect on the NAD$^+$. In this case, an (N,V,T) ensemble was used with a temperature of 300 K. The case where NAD and NAD$^+$ are positioned on the external surface of the tube was simulated within an (N,V,E), applying periodic boundary conditions for a virtually infinite SWCNT.

First, we considered the interaction of NADH and NAD$^+$ along the SWCNT (Figure 2). The NADH and NAD$^+$ dynamically evolved into the configurations shown in Figure 2 top and bottom. Although the NAD$^+$ was able to reorient around the tube and despite the use of an additional empirical force field to model the van der Waals interactions, no strong interactions were observed. Moreover, we could prove, giving a small initial momentum along the tube axis, that both NADH
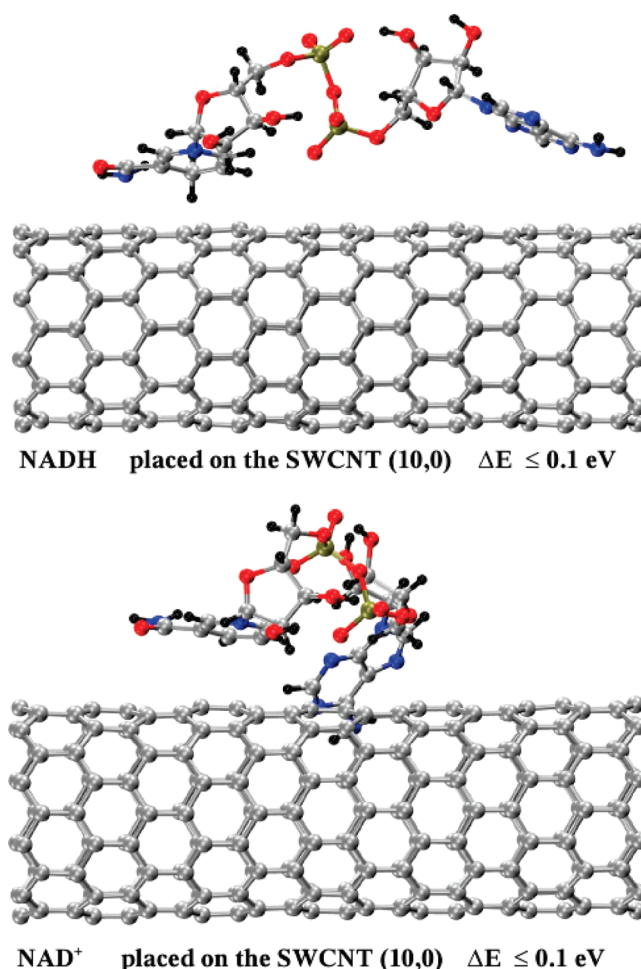
and NAD$^+$ can displace along the SWCNT with an energy barrier lower than 0.1 eV. Then, we placed the NAD$^+$ at the edge and allowed the system to evolve freely for about 5 ps, considering four different cases. In case (1), the edge was saturated with H atoms (Figure 3a), and the NAD$^+$ was positioned with the positive N$^+$ site close to the edge; after a few ps, the molecule detached from the edge. The estimated complexation energy turned out to be less than 0.1 eV. In case (2), the edge was saturated again with H, except for one COO$^-$ group (Figure 3b). In this case, the NAD$^+$ displaced to a closer distance, and the interaction was mostly electrostatic, with a complexation energy of 0.15−0.2 eV. In the cases (3) and (4), we saturated the edge with hydroxyl groups plus one COO$^-$ and oxygen atoms and one COO$^-$, respectively (Figure 3c and d). As expected, in case (3) (Figure 3c), the COO$^-$ formed a chemical bond with one H atom taken from one of the adjacent OH groups; as a result, the COO$^-$ lost part of its reactivity. In the end, although the NAD$^+$ positioned itself in order to optimize the global electrostatic interaction, the resulting complexation energy was about 0.2−0.3 eV. In case (4), where we have O atoms and one COO$^-$ (Figure 3d), some hydrogen bonds were
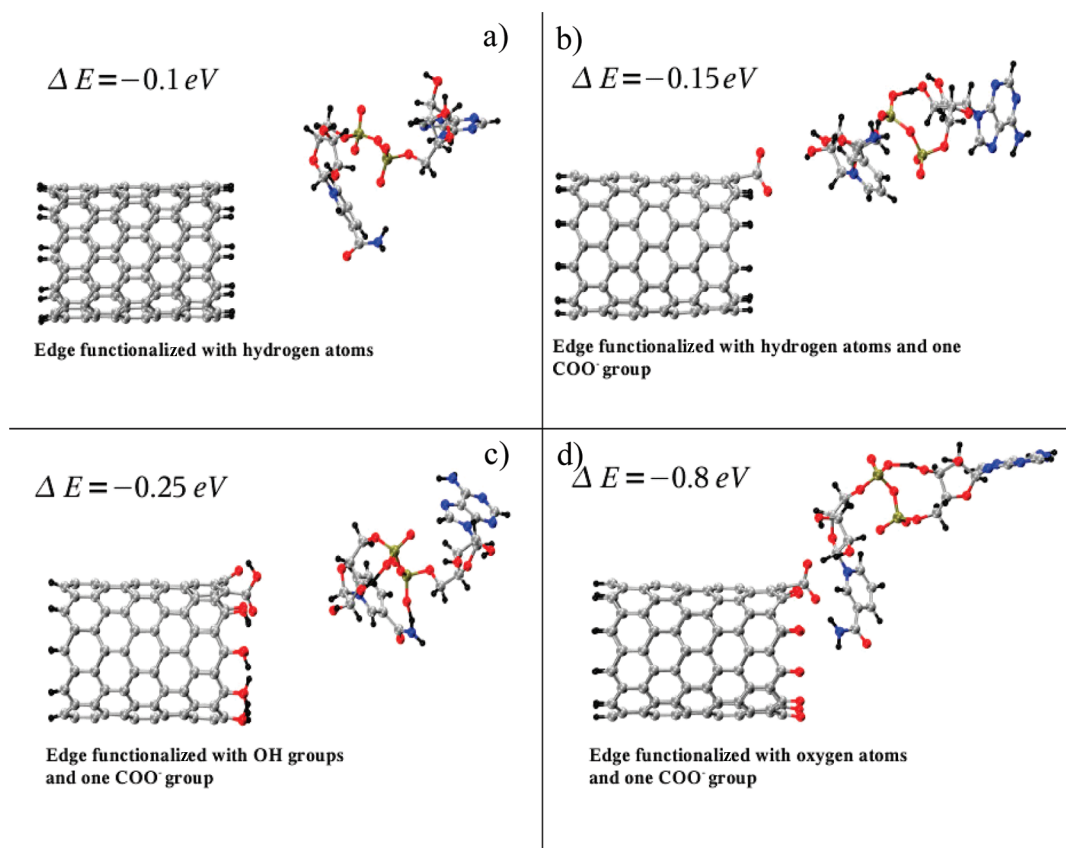
Figure 3. (a) Geometry of nanotube (10,0) saturated with H atoms at both ends with a NAD^+ at one edge and (b) with the edge on the right saturated with H atoms and one COO^- group. (c) Geometry of nanotube (10,0) with the edge saturated with hydroxyl groups and one COO^- group and (d) with the edge saturated with O atoms and one COO^- group (final geometries).

Table 1. Interaction Energies for the Various Systems Discussed in the Text As Computed from CPMD Simulations

system	ΔE_{int} (eV)
NAD, NAD^+ on the wall of the SWCNT	< 0.10
NAD^+ at the edge of the SWCNT terminated with H	0.10
NAD^+ at the edge of the SWCNT terminated with H and one COO^-	0.15
NAD^+ at the edge of SWCNT terminated with OH and one COO^-	0.25
NAD^+ at the edge of the SWCNT terminated with O and one COO^-	0.80

formed, and a stronger electrostatic interaction occurred. The NAD^+ was located remarkably close to the tube, and the estimated interaction energy was 0.8 eV (for more details see the Supporting Information).

These simulations indicate that NAD^+ strongly interacts with the edge of nanotubes, provided that the edge contains carboxylic groups, especially in the case of other O atoms present at the edge. The interaction energy was defined as

$$\Delta E_{int} = E_{SWCNT\ NAD+} - E_{NAD+} - E_{SWCNT}$$

We can see from Table 1 that this energy increases, as mentioned, in going from the H-saturated case to the case where both O atoms and one COO^- group are present at the edge.

In conclusion, in analogy with the case of NAD^+ on graphene,[17] our simulations show that the presence of carboxylic groups at the edge of a SWCNT, especially in combination with other groups, is responsible for a significant interaction between the NAD^+ and the edge of the single-walled nanotube, in agreement with the experimental outcome. No relevant interactions were observed when the NADH and NAD^+ were placed along the tube axis or close to the H-saturated edges of nanotubes. The study was done for nonmetallic tubes. However, we expect these results to hold also for metallic tubes. The investigation of this issue would require the use of a different approach, such as Born–Oppenheimer molecular dynamics, and will be the target of a forthcoming work. In combination with results from electrochemical experiments, it can be unambiguously concluded that the "resistance" toward passivation originates from the very large surface area of SWCNT-based electrodes, and it is not related to other inherent properties of carbon nanotubes, such as the electrocatalytic effect and high curvature. These findings can be extrapolated to the adsorption of molecules containing nicotinamide moieties, such as vitamin B3 or $NADP^+$.

SUPPORTING INFORMATION AVAILABLE Detailed experimental section. This material is available free of charge via the Internet at http://pubs.acs.org.

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