Lecture IX

PROBLEM 1
Estimate the increase in sensitivity, for hydrogen peroxide detection in cyclic voltammetry, after the functionalization of the working electrode with SWCNTs. Assume that the increase in sensitivity is only given by the increase in the electroactive area.
Consider electrode diameter of 4mm and a scan rate of 100mV/s. A solution of 1mg/ml of SWCNT in chlorophorm was prepared and then 10μl were drop cast on the electrode surface. Consider nanotubes as rigid bodies with diameter equal to 1.5nm and length 500nm.

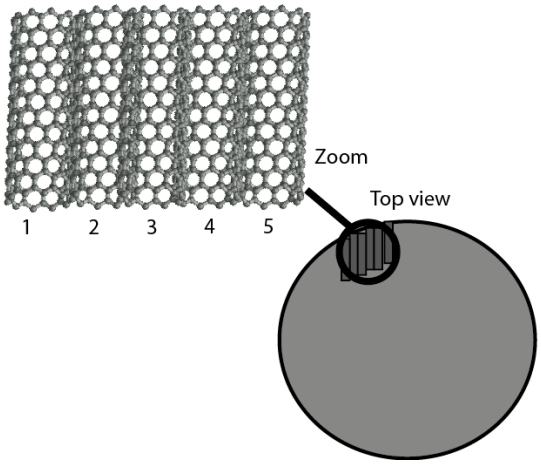
Solution
The electrode area, before the deposition of SWCNTs, is equal to 0.1256cm^2.
From Randles-Sevčik equation, we can estimate the theoretical sensitivity as

$$S = \frac{\Delta i}{\Delta C} = 0.446nFA\sqrt{\frac{nFDv}{RT}}$$

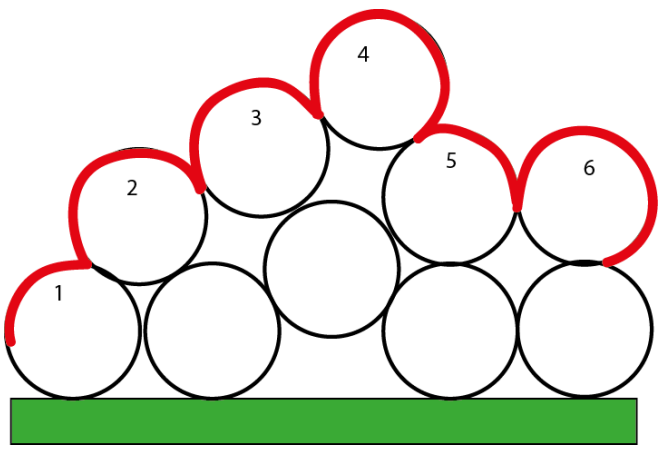
the only term that will change after deposition of SWCNTs is the area A. So, once we estimate the new area A' after the deposition, we will obtain the increase in sensitivity.

Main assumptions:
We consider carbon-nanotubes as rigid bodies, aligned on the surface of the electrode. We can approximate CNTs as a layer of small cylinders spread parallel on the electrode surface.

We can divide the electrode surface in small sections, each made by a bundle of CNTs:



We can calculate the area of each section, by assuming that the bundle of CNT has the following conformation



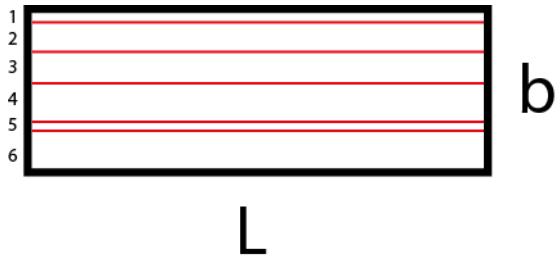
AREA OF EACH SECTION:

$$A_S = \left(\frac{1}{4}P + \frac{1}{2}P + \frac{1}{2}P + \frac{3}{4}P + \frac{1}{3}P + \frac{3}{4}P\right) \cdot L = 3.0833 \cdot \pi \cdot 1.5nm \cdot 500nm = 7265nm^2$$

where P is the perimeter of the single CNT, and L the length.

NUMBER OF SECTIONS

Let's consider the top view of the section:



The apparent area is equal to:

$$A_p = b \cdot L$$

Where b is:

$$b \approx 0.7nm + 1.3nm + 1.3nm + 1.5nm + 0.7nm + 1.5nm = 7nm$$

$$A_p = b \cdot L = 70nm \cdot 500nm = 3500nm^2$$

The number of sections can be estimated as:

$$\#sections = \frac{Area\ electrode}{A_p} = \frac{12.56 \cdot 10^{12}nm^2}{3500nm^2} = 3.6 \cdot 10^9$$

So the increase in sensitivity is equal to

$$\Delta S = \frac{S^1}{S} = \frac{A^1}{A} = \frac{3.6 \cdot 10^9 \cdot 7265nm^2}{12.56 \cdot 10^{12}nm^2} = \approx 2.1$$

PROBLEM 2

By nanostructuring electrodes with carbon nanotubes we obtained an increase in sensitivity (obtained with cyclic voltammetry measurements) from 0.26nA/μm mm^2 to 0.63nA/μm mm^2. Estimate the increase in the electroactive area in this case, starting from the Randles-Sevčik equation.

Solution

From Randles-Sevčik equation, we can estimate the theoretical sensitivity as

$$S = \frac{\Delta i}{\Delta C} = {}^{0.446nFA}\sqrt{\frac{nFDv}{RT}}$$

the only term that will change after deposition of CNTs is the area A. We can calculate the increase in the electroactive area as:

$$\frac{S^1}{S} = \frac{A^1}{A} = \frac{0.63}{0.26} \approx 2.43\ times$$