In this supplementary information the calculation procedures associated with the chosen model system, representing a “particle-in-a-box” which can undergo solvation, are discussed.

**Kinetic Energy levels (6e^T) of model armchair CNT system.** The CNT unit cell was defined by a single column of carbon atoms arranged in an armchair configuration connected periodically at the ends. This configuration is illustrated in Figure S1 as ribbons by the the pink box, which become an armchair nanoring when periodic boundary conditions are enforced. This unit nanoring cell, which can be repeated in space to generate a nanotube, was represented by a matrix α in the calculation. The interaction between the neighbouring unit rings in a tube was captured via the coupling matrix β_a. These two matrices, as shown in Figure S1 were used to build the hamiltonian H for a finite armchair CNT 5,6 whose kinetic eigenvalues, obtained via solving Schrodinger’s equation

\[ \epsilon^T \psi = H \psi \]  (1)

serve as the corresponding kinetic energy levels of that particular system. Here, \( \epsilon^T = \{\epsilon_1^T, \epsilon_1^T, ..., \epsilon_{N-1}^T, \epsilon_N^T, \epsilon_{N+1}^T, ..., \epsilon_Y^T\} \) has all the kinetic energies and \( \psi \) contains the corresponding wavefunctions. The total number of carbon atoms in a finite tube is \( N \) such that \( H \) is an \( N \times N \) matrix. This gives us the kinetic energy level structure of a CNT that contains critical information,
which contributes to the position of the current peaks during voltammetric characterization. We note, that although the tight-binding (TB) method is not self-consistent by nature, implementation of a first-principles self-consistent method to solve the large CNTs considered in this work would require a significant amount of computational resources. Moreover, we intend to demonstrate a general connection between the voltammetric output and the particle energetics, for which the inherent degree of accuracy of the TB method should suffice. The energy levels, representing a finite system are in principle a quantized subset of the energies obtained for the same tube of infinite length. This parent set forms the energy dispersion along the tube length with a fixed radius, which can be achieved via the general expression

\[ e^T(k) = \alpha + \beta e^{ikp} + \beta^* e^{-ikp} \]  \hspace{1cm} (2)

where \( p = 2b \) is the spacing between neighbouring armchair unit cells, as shown in Figure S1. The wave vector is given by \( k \) such that for an armchair tube \( k \equiv k_z = \frac{n_z}{N_zp} \) where \( n_z = 0,1,2,\ldots,N_z \).
$N_z$ being the number of armchair unit cells (rings) repeating along the $k_z$ direction. Beside the infinite case, eq 2 was used to examine the finite cases as well by restricting $N_z$ in accordance with the dimensions of the respective finite systems. This allows us to compare the analytical results with the discrete energy eigenvalues obtained via eq 1, which is discussed in detail in the next section.

**Figure S2:** Comparison between the analytically and numerically derived energy states for armchair nanotubes. Eq 9 was implemented for 14, 15, 16 unit cells and infinitely long (13,13) tubes generating the dispersions in part (a). The sampled, allowed values for a semiconducting (15 unit cells long) and a metallic (16 unit cells long) tube were isolated in part (b[i]) and (c[i]) respectively. The allowed states here, highlighted with red lines were compared with the respective TB derived energy levels in part (b[ii]) and (c[ii]) for the same geometries.

*Comparing electronic structures: analytical vs numerical.* Beside the numerical calculations via the TB method, we utilized eq 2 (above) to extract the electron kinetic energy dispersions for both infinite and finite nanotubes. This allows us to compare the energy levels obtained via the TB method with analytical solutions obtained via quantization of the Brillouin zone (BZ). The first comparison is presented in Figure S2 for the model (13,13) armchair nanotube. The dispersions in part (a) show that the allowed energies obtained through analytical quantization of the BZ at three different finite tube lengths ($L = [14 15 16] \times 2b$) are all subsets of the energy continuum generated by the *infinite* (13,13) nanotube. Two of these finite tubes are semiconducting [14 (red) and 15 (blue) unit cells] while the third one (16 unit cells) is metallic.
Since the states near the Fermi level $\varepsilon_F$ are of the greatest interest with respect to electrochemical spectra, we isolate the dispersions for the 15 (semiconducting) and 16 (metallic) unit cell long tubes and compare the respective electronic structures near $\varepsilon_F$ with those produced via the TB method for identical armchair geometries. Part (b) of Figure S2 shows this contrast for the 15 unit cell long tube where we see a close match between the energies derived analytically (b[i]) and numerically (b[ii]). A similar outcome follows with the 16 unit long, metallic tube in Figure S2(c), where the analytical (c[i]) and numerical (c[ii]) results display a satisfactory match. The slight mismatch here arises from the boundary condition imposed on electrons by finite CNTs. This imbalance, as shown in the paper, translate into the electrochemically extracted energy dispersion profiles (see Figure 8b of manuscript). This picture suggests that the TB derived electron kinetic energies for the finite armchair tube lengths are likely to be quantized constituents of the continuous electron kinetic energy spectrum of an infinitely long nanotube.

**Reversal of electronic structure in finite nanotubes.** Typically infinite armchair tubes appear to be metallic at all tube lengths. However, finite tubes are predicted in Figure 4 of the manuscript to be of mixed semiconducting and metallic characters. This shift in armchair CNT’s electronic structure for finite tubes can be attributed to the quantization of the 2D Brillouin zone of the CNTs along both the armchair ($k_a$) and zigzag ($k_z$) directions (Figure S1). To understand this, let us consider armchair nanotubes with a constant radius. On the one hand, the fixed number of armchair units (shown in the green box in Figure S1 of the manuscript) within the unit nano-ring cell specifies the number and positions of the allowed $k$ values along the $k_a$ direction in the BZ. These allowed values can be obtained via $k_a = \xi_a(2\pi/2n_a)$, where $\xi_a$ is an integer, $n_a$ is the armchair chiral index as in $(n_a, n_a)$. One of these allowed $k$ points always conform with the $\Gamma'(0,0)$ point irrespective of the assumed tube radius and thus passes through the Dirac point $(0,2\pi/3b)$ in the BZ. The allowed $k$ values in the $k_z$ direction on the other hand, are determined by the tube length which is a variable in this analysis and depends on the number of unit armchair nanorings. The neighboring rings in the tube are spaced by the unit vector of length $2b$ along the $y$ (zigzag) direction, which gives the corresponding allowed values via $k_z = \xi_z(2\pi/2n_z)$. Here, $\xi_z$ is the integer defined above, $n_z$ is the zigzag chiral index utilized in this context to specify the length of the armchair nanotube. Just as before, one of these allowed values through $\{\xi_z\}$ conforms with the Dirac point when $|n_z|/3 \equiv (\xi_z - 1)/3 = 1$. Lengths that satisfy this condition display metallic property, otherwise the nanotube is semiconducting. This interpretation compliments the results shown in Figure 4 of the manuscript for finite armchair tubes.
**Extraction of energy dispersion.** As highlighted in the manuscript, the extraction requires the identification of the lowest unoccupied level $\varepsilon^T_{\nu}$ above $\varepsilon_F$ using the first two peak potentials for a series of nanotube lengths. A change in the length of the (13,13) nanotube would correspond to a change in the number of allowed $k$ points along the $k_z$ direction via $k_z = n_z L = n_z \pi / 2b N_z$, where $2b$ is the distance between the neighbouring armchair nanoring units (Figure 8 of the manuscript). For a given length to be metallic, one of the allowed values must coincide with the Dirac point at $k_z = 2\pi / 3b$, which requires satisfying the condition $n_z / N_z = 4 / 3$. At this point $(0, 2\pi / 3b)$, the subband energy is going to be zero. In the context of the nano-ring based unit cell representation, we already established that a metallic tube will consist of $3\xi_z + 1$ unit rings, where $\xi_z$ is an integer. For example, when the number of unit cells in (13,13) CNTs are 4, 7, 10, 13, ... etc., then $e^T(2\pi / 3b) = 0$ and the tubes will be metallic. Thus, tubes with $L$ corresponding to $3\xi_z + 2$ and $3\xi_z + 3$ are semiconducting. Since The $k$ values for the semiconducting lengths do not coincide with the Dirac point, the lowest energy above $\varepsilon^T = 0$ can be expected to lie at the $k$ points immediately neighboring the Dirac point. This neighboring $k$ point lies above $k_z = 2\pi / 3b$ for $L/2b = 3\xi_z + 2$ and below $k_z = 2\pi / 3b$ for $L/2b = 3\xi_z + 3$. Hence the immediately neighboring $k$ values corresponding to the minimum energies for $L/2b = 5, 8, 11, 14, ...$ etc occur at $k_z = 3\pi / 4b$, $5\pi / 7b$, $7\pi / 10b$, $9\pi / 13b$, ... etc respectively, all of which lie on the right-hand side of the Dirac point $(0, 2\pi / 3b)$. Similarly, for $L/2b = 6, 9, 12, 15, ...$ etc. the minimum energy should appear at $k_z = 3\pi / 5b$, $5\pi / 8b$, $7\pi / 11b$, $9\pi / 14b$, ... etc respectively, which lies on the left of $2\pi / 3b$. The minimum energies were collected via voltammetric simulations based on methods discussed in the manuscript and then matched with the corresponding $k$ points immediately neighboring the Dirac point.

**References**


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