Effect of the electronic structure of carbon nanotubes on the selectivity of electrochemical functionalization

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Supporting Information

Figure S1: In situ conductance profiles while performing ECM at a (a) metallic nanotube and (b) a semiconducting nanotube whose characteristics are summarized in figure 3. The experiment is initiated by placing a water droplet over the contacted tube and inserting a Ag/AgCl wire. The tube conductance is then monitored as a function of the applied gate voltage (V_{lG}). Following this 10mM DDA with 50 mM LPC in water is added during the first cycle when the voltage reaches a value marked by the arrows in the figures. The maximum positive voltage scanned is increased in every cycle. In (a) when V_{lG} reaches approx. 0.25 V, the conductance decreases drastically signifying a high degree of coupling to the metallic nanotube. However, in (b) no clear change in transport characteristics is observed signifying a low extent of functionalization. It can also be observed that during the fourth and subsequent cycles the whole curve shifts to lower conductance values in both cases.

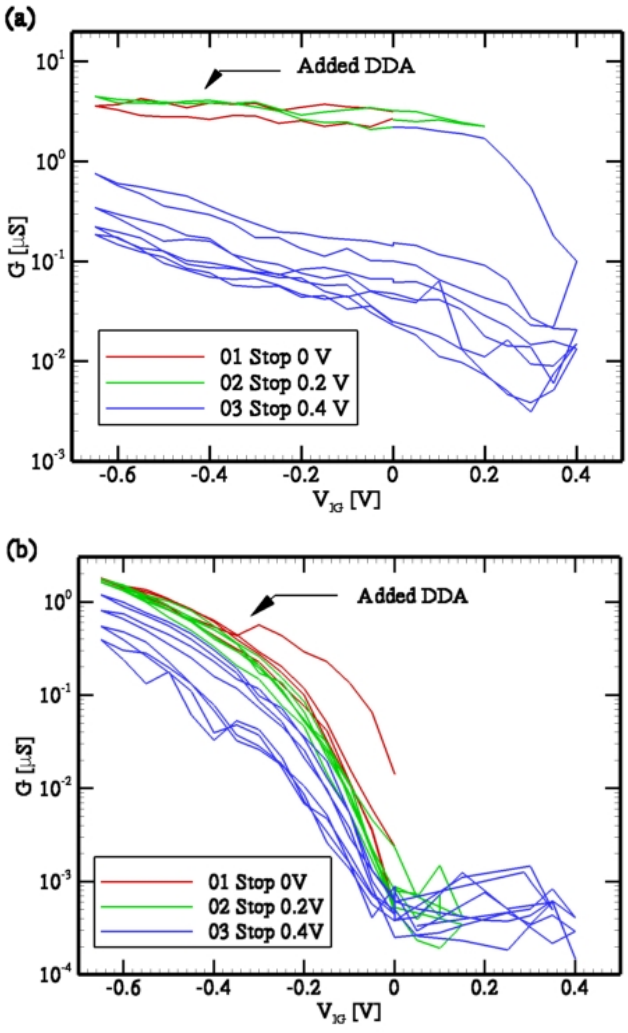
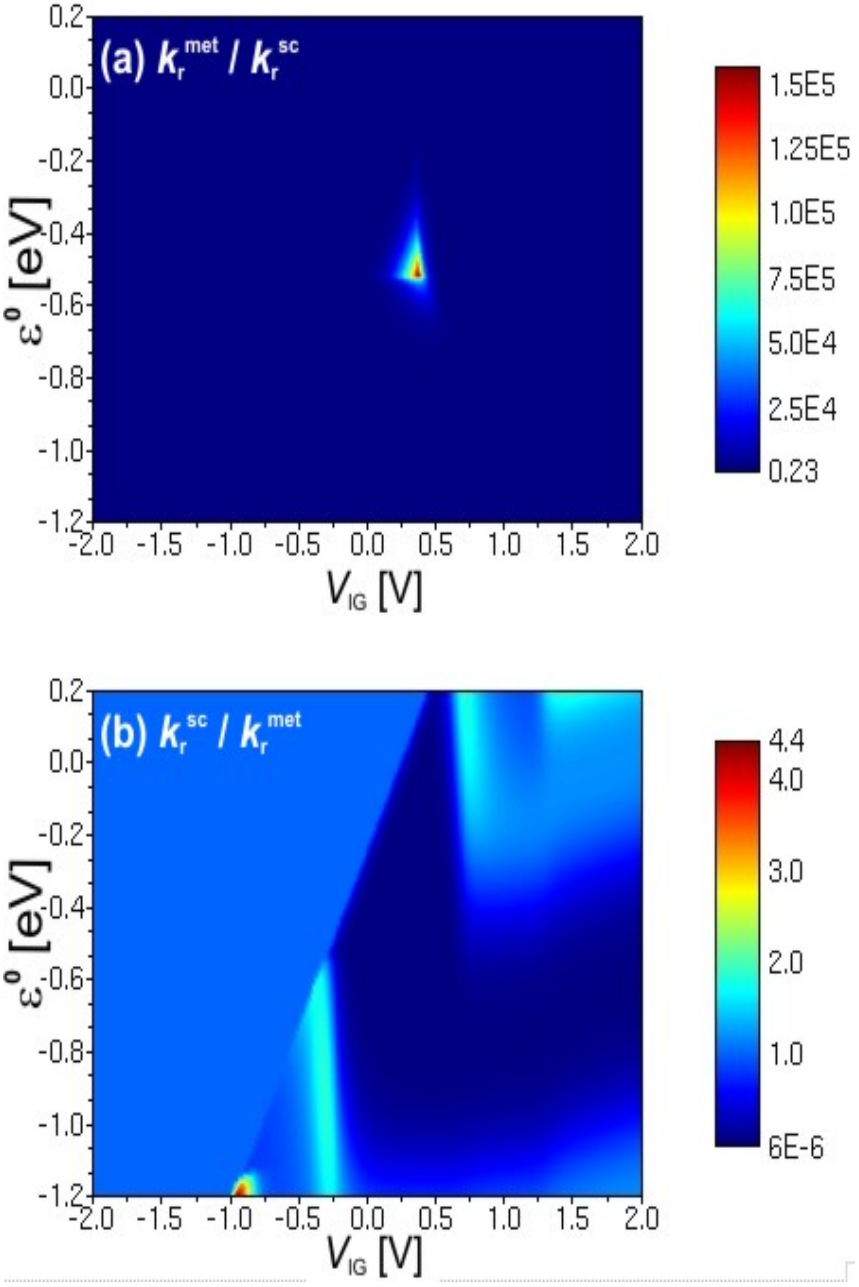


Figure S2: Coupling efficiency maps as a function of the formal potential of redox couple (ε^0) and the applied gate voltage (V_{appl}): (a) k_r^{met}/k_r^{sc} metallic coupling ratio (b) k_r^{sc}/k_r^{met} semiconductor coupling ratio. For both cases, λ = 1 eV and V_{hf} = 0.2 V. In (a) the red regions signify the situation where the coupling is maximized at a (9,0) tube with respect to a (10,0) tube. While in (b) the red regions signify an increased coupling at the semiconducting tube with respect to the metallic one.



Comparison of reduction rates at the (9,0) and (5,5) tube

Using the same methodology as outlined in the paper, we have also calculated the reduction rates at a (5,5) (arm-chair) tube and compared it with that at the (9,0) zig-zag tube. From the figures presented below (figures S3 to S6), it is apparent that there is hardly a difference in reactivity between the two tubes. This serves as a support to validate our calculations and suggests that the difference in reactivity mainly arises due to the variation in the electronic structure.

Figure S3 : Calculated k_r curves at the (9,0) and (5,5) tubes (please compare **figure 4**). Vappl ≡ V_{lG}, Ezero ≡ ε^0.

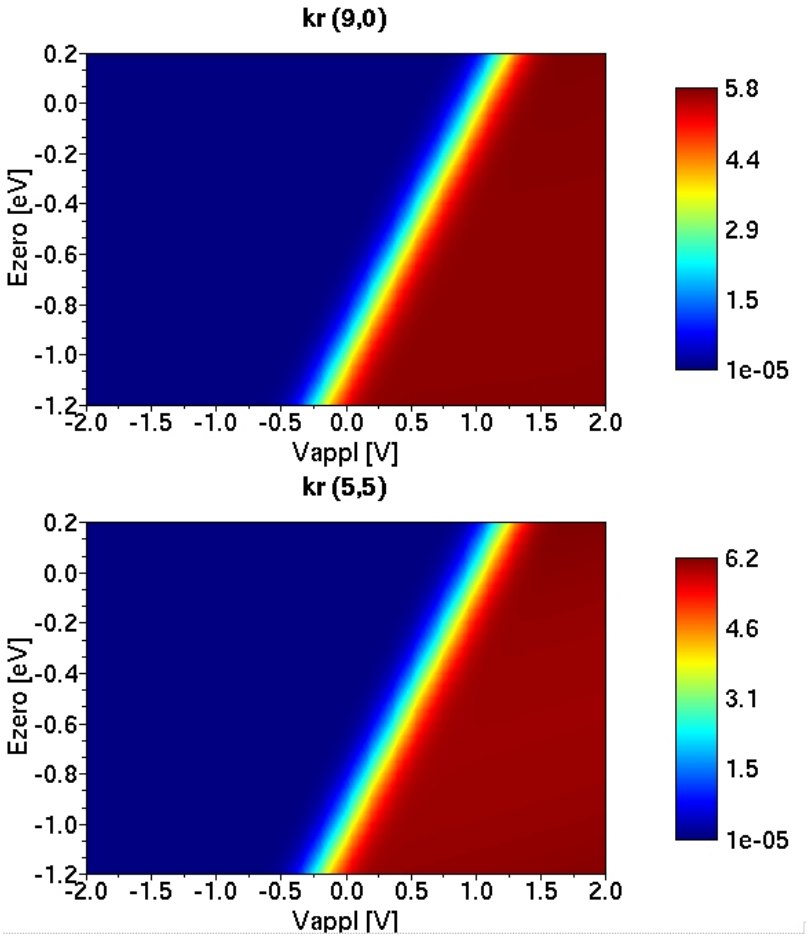


Figure S4: Comparison of the calculated k_r curves between the (9,0) and (5,5) tubes for specific formal potentials of Ezero ≡ ε^0 = -0.6 eV and -0.25 eV. Vappl ≡ V_{lG}. (Please compare **figure 5**).

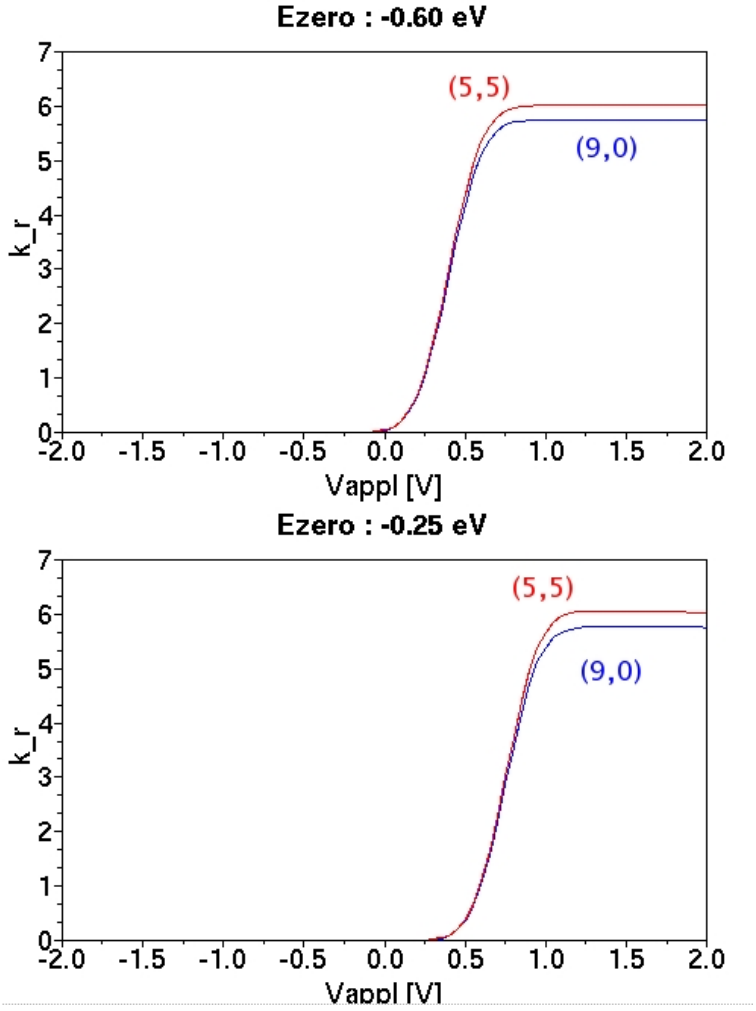


Figure S5: Calculated zig-zag coupling efficiencies ($k_r(9,0)$ / $k_r(5,5)$) for various formal potentials (Ezero ≡ ε^0). Vappl ≡ V_{lG}. (Please compare **figure 6**).

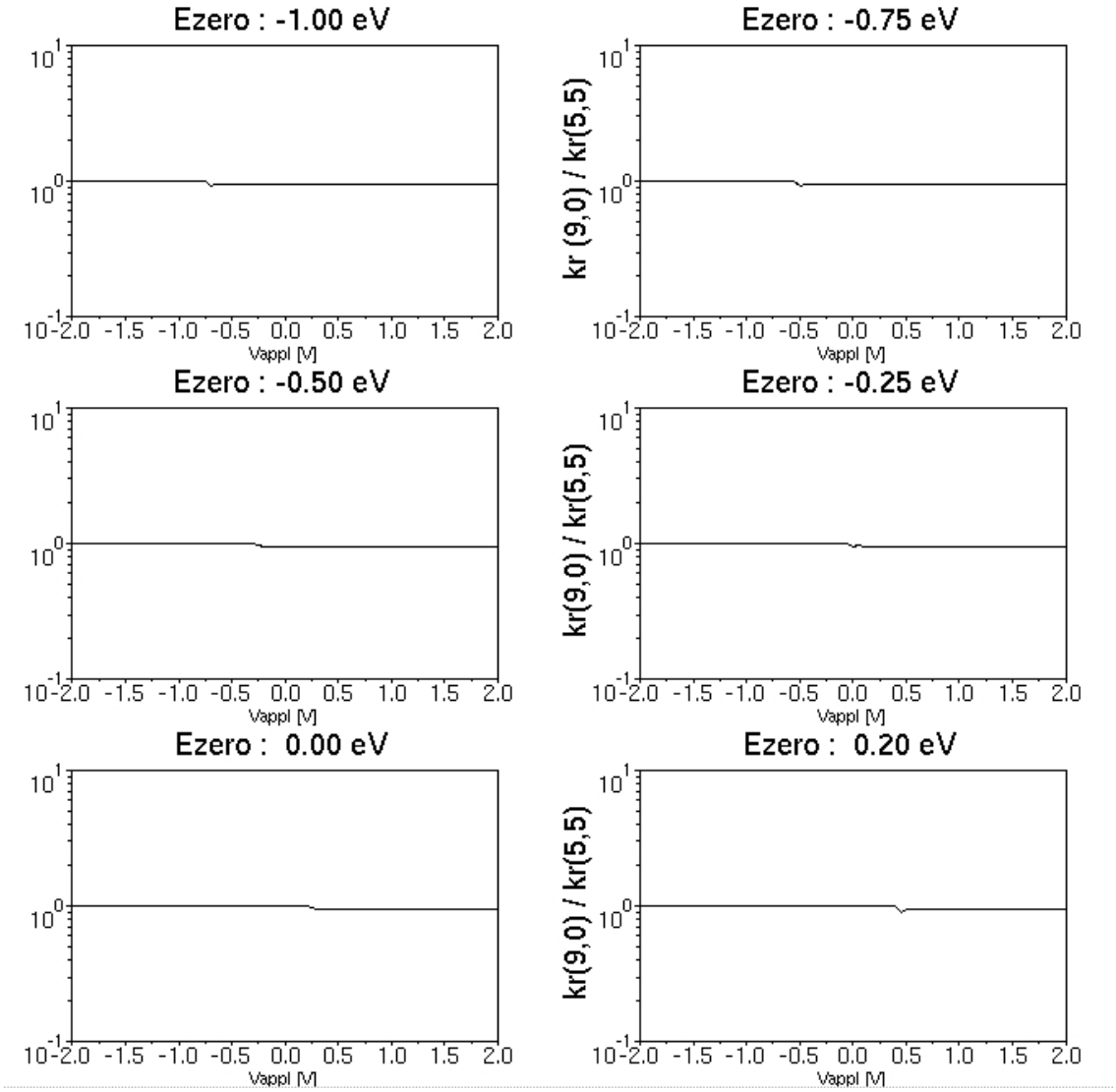
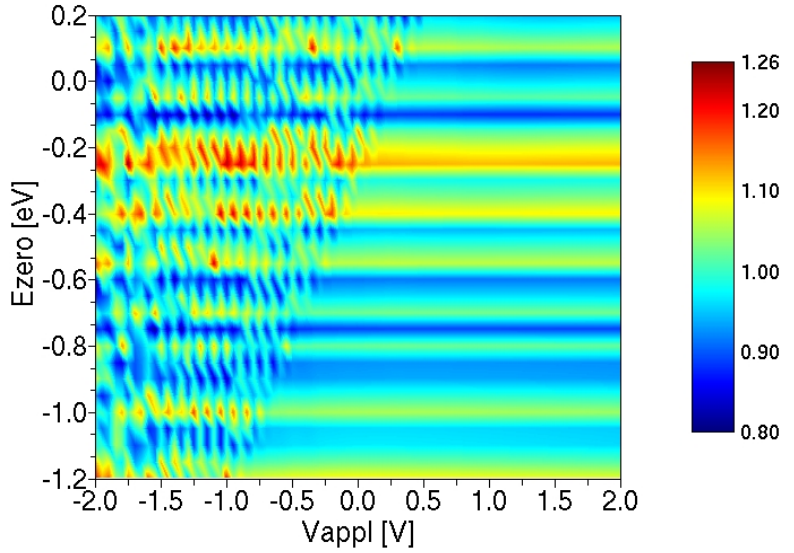


Figure S6: Map showing the coupling efficiencies: (a) (***k*_r(9,0) / *k*_r(5,5)**) and (b) (***k*_r(5,5) / *k*_r(9,0)**) as a function of the gate voltage (Vappl ≡ V_{IG}) and the formal potential (Ezero ≡ ε^0). (Please compare **figure S2**).

(a) $k_r(9,0) / k_r(5,5)$



(b) $k_r(5,5) / k_r(9,0)$