EFFECTS OF O_2 AND Cs ADSORBATES ON FIELD EMISSION PROPERTIES IN SINGLE-WALL CARBON NANOTUBES: A DENSITY FUNCTIONAL THEORY STUDY

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Recently, carbon nanotubes (CNTs) attracted considerable attention for field emission (FE) applications, due to their capability of emitting high currents (up to 1 A/cm^2) at low field (~ 5 V/μm)[1]. Indeed, advances in the production of well-aligned carbon nanotubes, and control over their deposition, made it possible to use CNTs as potential emitters[2]; a prototype of a flat panel with color display[3] has already been achieved. Notwithstanding the rapid technological progress, there are still unanswered questions in terms of the emission mechanisms of CNTs. The field emission properties have previously been explained in terms of Fowler-Nordheim's (FN) theory[4], which suggests that the emission occurs by a tunneling process. However, recent experiments[5] show a deviation of the current-voltage (I-V) characteristics from the FN model. Saito et al.[6] suggested that the deviation is due to the nonmetallic local density of states present at the tips, while Bonard et al.[7], reported that this deviation results from the interaction between tubes; other reports suggest the deviation to occur due to gas adsorption at various CNTs sites[8].

Experimental[8,9] studies of the effects of O_2 adsorption on CNTs show current suppression, while a current enhancement was observed for Cs deposition on CNTs[10]. In this work, we present a comprehensive theoretical study on the effects of O_2 and Cs adsorbates on the field emission properties of CNTs, investigating the adsorption mechanisms of O_2 and Cs at the tips of capped and uncapped C(5,5) CNTs using all-electron LCAO density functional theory calculations, with a double numerical polarized basis set in Dmol3[11]. A uniform external field (EF) directed from the top toward the tube-tip was applied, in order to simulate the emission environment. The geometries of the systems considered were optimized in the absence and presence of an electric field. Structural and electronic properties will be discussed in detail. We also report on the effects of the applied field on the reaction mechanisms.

Our preliminary calculations show a current suppression upon O_2 adsorption. Table I lists the results of the first ionization potentials (IP) and the highest occupied molecular orbitals (HOMO) of the various configurations, shown in Figure I. Upon O_2 adsorption, and in the absence of an electric filed, no effect on the IP is observed in config.–A, with respect to the bare-tube, while an increase is noted for the intermediate and final configurations, namely config.–B and config.–C, respectively. The corresponding HOMO energies of the considered configurations are consistent with the IPs. However, under an 1 eV/Å applied field, the IP increased about 5% in configs.–A and –B, and 9% in config.–C, upon O_2 adsorption. This result implies that an applied field exacerbates the current suppression. A similar study is being carried out for the capped carbon nanotube, in order to study the role of Cs in the current enhancement.

Our preliminary results identified the adsorption sites that contribute to the current suppression upon O_2 adsorption. An applied field is shown to exacerbate this current suppression and lowers the adsorption energies. Full analysis of our results will be presented, which entail configurations of the capped nanotube and the effects of Cs adsorbates.

Table I: CNTs with O_2 adsorbates ionization potentials and HOMO (in eV) energies of *uncapped* carbon nanotube.

EF	0.0 eV/Å		1.0 eV/Å	
	IP	HOMO	IP	HOMO
Bare-tube	6.200	-4.809	6.650	-5.370
Config. A	6.200	-4.816	7.000	-5.626
Config. B	6.340	-4.955	7.000	-5.623
Config. C	6.340	-4.929	7.330	-5.913

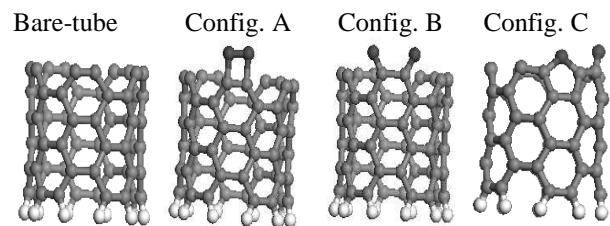Bare-tube   Config. A   Config. B   Config. C

Figure I: O_2 adsorption sites for an uncapped nanotube.

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