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Reduced backscattering in potassium-doped nanotubes: *Ab initio* and semiempirical simulations

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By means of combined *ab initio* and semiempirical simulations, the charge transmission properties of potassium- and nitrogen-doped nanotubes are compared. The backscattering efficiency of adsorbed potassium is shown to be much weaker, owing to a shallower impurity potential well that weakly traps the induced quasibound states. The difference in conductance and elastic mean free paths is further investigated for nanotubes with lengths of several tens of micrometers and random distribution of dopants. Our results provide clear criteria for favoring doping by physisorption instead of chemical substitutions.

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I. INTRODUCTION

The integration of carbon nanotubes (CNTs) in electronic devices such as field-effect transistors (CNFETs) (Ref. 1) has generated much experimental and theoretical work to understand the basic phenomena controlling the device performances. As a crucial ingredient, the doping of the semiconducting canal has been achieved following different strategies. In particular, with the early synthesis of composite $B_xC_yN_z$ nanotubes,[2] substitutional doping by boron or nitrogen, and its consequences on the structural,[3–5] electronic,[6,7] and transport properties,[8–11] have been extensively studied.

While substitutional doping certainly increases the carrier density in the CNTs, it also induces significant backscattering that can reduce the charge transmission capability of a given conduction channel. This has been clearly demonstrated on the basis of tight-binding[12–14] or *ab initio*[15,16] calculations for isolated impurities and randomly N-or B-doped metallic tubes.[7,14]

As an alternative to substitutional doping, several recent experimental reports showed that *n*-type CNFET based on potassium (K) doped semiconducting tubes[17–22] can display performances comparable to the best *p*-type CNFET. Further, the ability of K atoms to push the Fermi level into the conduction bands leads to the possibility of "multimode" transport in nanotubes.[19] An enhanced hydrogen uptake[23] and a transition from Luttinger to a Fermi liquid behavior[24] have also increased the interest in K-doped nanotubes.

In this paper, we study the conductance of metallic and semiconducting tubes doped either by K in adsorption or N in substitution. A recently developed O(N) *ab initio* method is used to precisely compute the effect of isolated defects on the Landauer transmission. Our *ab initio* results are further used to construct an accurate π-π^* effective model that allows us to access, within the Kubo formalism, the conductance and elastic mean free path of tubes randomly doped over micrometer scales. When compared to N, the scattering effects induced by K atoms are shown to yield much less backscattering, with resulting longer mean free path and charge mobilities.

II. THEORETICAL FRAMEWORK: AN *AB INITIO* O(N) TRANSPORT APPROACH

Our theoretical framework proceeds as follows. We start with a ground-state calculation of the system of interest (device and surrounding electrodes) using the SIESTA package, a density functional theory (DFT) code based on the use of strictly localized atomiclike orbitals.[25] The locality of the basis and the local density approximation lead to the partitioning of the system into "nearest-neighbor" sections (Fig. 1) so that the Hamiltonian H and overlap S matrices are tridiagonal by blocks. This property allows us to calculate with an O(N) scaling the Green's function of the system. The computational scheme is similar to standard tight-binding implementations of transport[26] but with submatrices replacing the scalar on-site and hopping terms. The Green's function of the "device" (notations of Fig. 1) reads

$$\hat{G}_D(\epsilon) = [\epsilon\hat{S}_D - \hat{H}_D - \hat{\Sigma}_L(\epsilon) - \hat{\Sigma}_R(\epsilon)]^{-1}, \tag{1}$$

$$\hat{\Sigma}_L(\epsilon) = [\hat{T}_{LD} - \epsilon\hat{S}_{LD}]^{\dagger}\hat{G}_{00,L}(\epsilon)[\hat{T}_{LD} - \epsilon\hat{S}_{LD}] \tag{2}$$

with Σ_L (Σ_R) the self-energy operator accounting for the interaction of the device with the left (right) electrode. The bulk "surface" Green's function ($\hat{G}_{00,L}$ for the left electrode), which is the restriction of the semi-infinite electrode Green's function to the electrode subsection in contact with the device area, can then be calculated iteratively as follows:

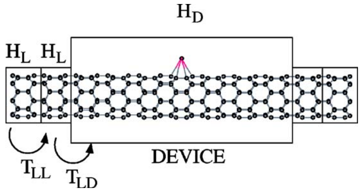

FIG. 1. (Color online) Symbolic representation of the partitioning of the studied systems into device and bulk areas yielding a block-tridiagonal representation of the infinite system Hamiltonian and overlap matrices.

$$\hat{G}^{(n+1)}_{00,L}(\epsilon)=[\epsilon\hat{S}_L-\hat{H}_L-\hat{U}^{\dagger}\hat{G}^{(n)}_{00,L}(\epsilon)\hat{U}]^{-1} \qquad (3)$$

$$\text{with } \hat{U}=[\hat{T}_{LL}-\epsilon\hat{S}_{LL}]^{-1} \qquad (4)$$

$$\text{and } \quad \hat{G}^{(0)}_{00,L}(\epsilon)=[\epsilon\hat{S}_L-\hat{H}_L]^{-1}. \qquad (5)$$

The energy-resolved transmission then reads $T(\epsilon)=\mathrm{Tr}(\hat{\Gamma}_L\hat{G}^a_D\hat{\Gamma}_R\hat{G}^r_D)$ with, e.g., $\Gamma_L=\mathrm{Im}(\hat{\Sigma}_L)$. Similar techniques are used to partition the device in nonoverlapping sections so as to calculate $\hat{G}_D$ and the transmission T within a strictly O(N) technique. The present approach is restricted to the linear response but allows us to study from first-principles systems containing several thousand atoms. More details about the present implementation will be presented elsewhere.[27–29]

At the ground-state level, the system (device+leads) can be repeated with periodic boundary conditions or terminated on each side by passivated buffer sections. Rather than imposing the electrode bulk potential or density in the lead sections, the length of the device is increased until achieving convergency of the transmission. The atomic positions are fully relaxed upon introduction of the impurity. A double-ζ (DZ) basis is used for C and N (two sets of s and p orbitals) and K atoms. In the case of K doping, the most stable impurity position is located ~2.4 Å above the center of a hexagon.[30]

III. SCATTERING BY ISOLATED DEFECTS

First, the case of a metallic C(6,6) nanotube is considered. The device contains up to 11 carbon sections (~27 Å) plus four sections on each side for the electrodes. Periodic boundary conditions are used for building the ground-state H and S matrices. The transmission of the ideal nanotube is calculated using the on-site $\hat{H}_L$ and hopping $\hat{T}_{LL}$ blocks associated with the four leftmost tube sections (see Fig. 1). The quality of the associated transmission plateau [Fig. 2(a)] is a clear indication that the selected device is large enough to recover the bulk properties in the leftmost (or rightmost) sections.

The case of substitutional N doping in armchair tubes was first investigated[15] using a plane-wave phase-matching approach. In excellent agreement with this previous work, we observe strong backscattering at the resonance energies of the donor "quasibound" states associated with the defect potential well. Two structures clearly emerge associated, respectively, with the "p-like" donor level just below the first van Hove singularity (vHs) in the conduction bands, and an "s-like" broad structure at lower energy (more bound).[15]

In the case of K doping, an important outcome of the present study is *the complete disappearance of the broad structure associated with the low energy (more bound) resonance state*.[31] In particular, around the charge neutrality point, and over a much larger range of energy on the lower plateau, the transmission is that oaf the ideal tube. This is a clear indication that K-doped tubes, as compared to the N-doped systems, will display a ballisticlike behavior on a much larger gate-voltage range and for longer propagation length of charge carriers.

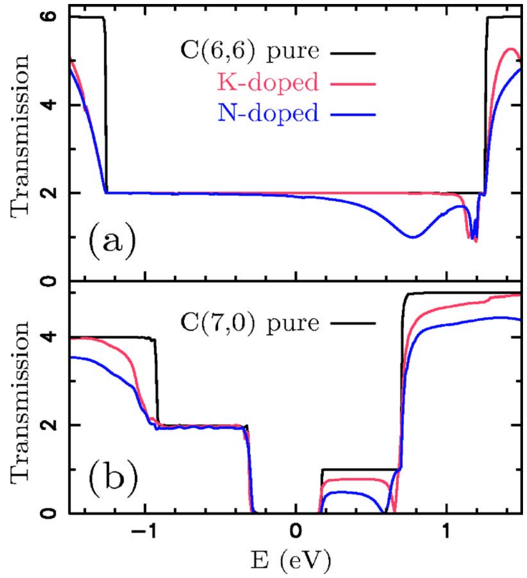

FIG. 2. (Color online) Transmission for (a) a C(6,6) and (b) a C(7,0) nanotube. Undoped (black), nitrogen-doped (blue), and potassium-doped (red) tubes are considered.

To understand the disappearance of the low energy resonance, we reproduce in Fig. 3 the evolution of the *ab initio* on-site Hamiltonian matrix elements associated with the p_z orbitals (perpendicular to the plane of atoms) as a function of the distance to the impurity in a doped (12×12) graphene sheet.[32] The potential well created by N in substitution is clearly much deeper than the one associated with the partially screened K$^+$ ion. In particular, the ability of adsorbed K ions to trap electrons is significantly reduced as compared to N impurities. We note that even though screening is ineffective in 1D systems, the K-induced potential does not seem to be much longer range than that generated by N and it is not clear that it presents a Coulomb-like shape.[33]

We also address the case of semiconducting tubes. The device consists of 12 C(7,0) tube sections connected by two sections on each side to mimic the bulk. The quality of the transmission plateau [Fig. 2(b)] associated with the on-site

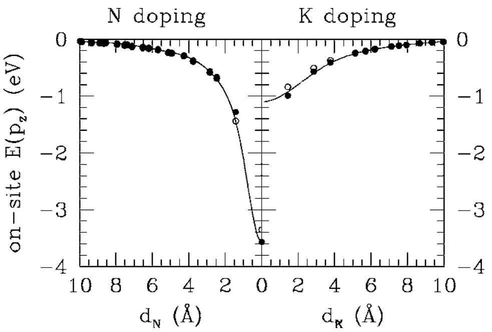

FIG. 3. On-site p_z orbital energies in the doped graphene sheet upon (left) N doping and (right) K doping. Filled and open circles correspond to the two p_z orbitals in the DZ basis and the solid line to the Gaussian fit. The abscissa indicates the distance (in Å) from a carbon atom to the impurity in the N case, and to the hexagon center on which the impurity projects in the K case.

and hopping Hamiltonian blocks of the two leftmost sections guarantees that the device is long enough to naturally recover bulk properties.[34] The conductance as a function of energy for an isolated N or K impurity is compared. Again, the backscattering is significantly reduced in the K case as compared to the N one, regardless of the carrier energies.

IV. SCATTERING BY A RANDOM DISTRIBUTION OF DOPANTS

A. Tight-binding parameters from *ab initio* results

To further substantiate the modifications of the transport length scales upon doping, one needs to investigate more realistic cases of micrometers-long nanotubes doped by a random distribution of scatterers. Rather than working with the full DZ basis, we observe that the on-site energies provided in Fig. 3 are precisely what is needed to build a simple π-π^* Hamiltonian with accurate parameters obtained directly from the self-consistent DFT calculations. To do so, the data points in Fig. 3 are fitted by a Gaussian-like functional form (solid lines).[35] In the π-π^* approach, the on-site energies (zero for unperturbed atoms) are then straightforwardly changed according to the Gaussian fits around impurity centers randomly distributed along a (10,10) nanotube. Concerning the off-diagonal coupling energies, inspection of the DFT Hamiltonian shows that they are remarkably stable around the impurity and equal within ~0.1 eV to the undoped tube value (γ_0=2.9 eV).

B. Tight-binding Kubo approach to transport

Even with an O(N) implementation, the computation of the transport properties with *ab initio* techniques still remains a challenge. To address the case of μm-long tubes doped by random scatterers, we abandon the Landauer picture used above to adopt a Kubo formalism implemented in real space[36] and exploiting the model Hamiltonian built in the previous subsection. Such a scheme has proven very powerful in studying the electronic diffusion properties in random media. The resolution of the time-dependent Schrödinger equation is performed by expanding the evolution operator $e^{-i\hat{\mathcal{H}}t}$ on a basis of orthogonal polynomials. The electron diffusion coefficients $D(E,t)$ are calculated[36] as a function of time t and energy E from

$$D(E,t) = \frac{X^2(E,t)}{t} = \frac{1}{t}\frac{\mathrm{Tr}[\delta(E-\hat{\mathcal{H}})[\hat{\mathcal{X}}(t)-\hat{\mathcal{X}}(0)]^2]}{\mathrm{Tr}[\delta(E-\hat{\mathcal{H}})]},$$

where $\delta(E-\hat{\mathcal{H}})$ is the spectral measure operator, whose trace gives the total density of states $n(E)$. The computation of $X^2(E,t)$ allows us to distinguish the different conduction regimes (ballistic, diffusive, or localized) and enables us to estimate the elastic scattering time τ beyond which the propagation becomes diffusive, namely $X^2(E,t)/t \sim \ell_e v_F$ for $t \gg \tau$, with v_F the Fermi velocity and ℓ_e the elastic mean free path (MFP). The Kubo conductance is then evaluated from $G(E,t)=2e^2/L(t)\mathrm{Tr}[\delta(E-\hat{\mathcal{H}})]D(E_F,t)$, in which $L(t)$ is the propagation length at time t.[36]

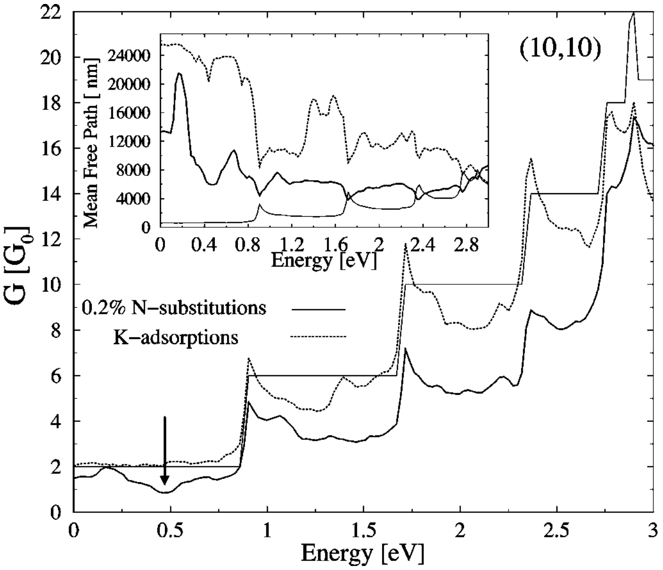

FIG. 4. Main frame: Conductance for the (10,10) nanotube with 0.2% of randomly substituted N impurities (bold) or physisorbed K impurities (dotted line). The number of quantum channels is also reported (solid line). Inset: Corresponding mean free paths together with the rescaled density of states (solid line).

Such calculations have been carried on doped (10,10) CNTs, containing from 0.1% to about 1% of nitrogen substitutions or K adsorbants. The Kubo approach within its π-π^* implementation allows us to study μm-long systems without the need to impose periodic boundary conditions so that the distribution of dopants can be chosen to be completely random. The total perturbation on a given carbon atom is taken to be the superposition of that created by all impurities. This approximation is certainly valid in the limit of low doping, which is the limit we study. For the (10,10) metallic tube with N impurities, one first verifies that our parametrization reproduces well the low density *ab initio* results as given by the peak in the density of states located at ~0.4–0.5 eV.[15]

C. Conductance and mean free path of doped μm-long tubes

In Fig. 4, the conductance (main frame) and the MFP (inset) for the (10,10) conducting tube with either N substitutions (bold line) or K adsorbants (dotted line) are reported. The density of impurities here is 0.2%. The chosen evolution time is $t \sim 15\,000\hbar/\gamma_0$ and the total length of the nanotube used for the calculation is larger than 20 μm, thus safely avoiding boundary effects.[36] Clearly, on the first plateau, *the effect of K impurities seems negligible when compared to N dopants*. More precisely, the MFP of the K-doped nanotube ($\ell_e \sim 24$ μm) is found to be four times larger than the N-doped tube at $E_F \sim 0.5$ eV (energy of the deeper N quasibound state), and at the same impurity density. For higher energies, the backscattering is enhanced for both types of doping, but still with a more significant impact in the case of substitutional doping.[37]

One should note that the performances of CNFETs are not uniquely determined by the value of the intrinsic conductance. Indeed, the modification of the contact resistance upon doping, by tuning the contribution of the superimposed Schottky barrier, may also play an important role.[38] Notwithstanding, the shortening of the MFP, and the resulting reduced charge mobilities, will strongly impact on the on-current capability of the CNFETs. Our results demonstrate that despite the (partly screened) electrostatic field produced by the K+ counterion, doping by charge transfer from adsorbed atoms or molecules will decrease charge-carrier mobilities much less than chemical substitution or covalent functionalization of the nanotube skeleton.[39]

V. CONCLUSIONS

In conclusion, the relative backscattering efficiency of substitutional versus physisorbed impurities has been studied on metallic and semiconducting tubes in the case of potassium and nitrogen doping. On the basis of *ab initio* conductance calculations, K impurities have been shown to induce much less backscattering as compared to nitrogen substitutions. By mapping the *ab initio* Hamiltonian onto a reduced π-π^* model, the conductance and mean free path of randomly doped micrometers-long tubes was investigated within the Kubo formalism, confirming that K doping leads to much longer mean free paths. Our results offer a clear motivation for selecting impurity or molecule physisorption over chemical functionalization in transistor-based applications.

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[31] The less bound resonances seem to coincide in the case of N and K doping of the C(6,6) tube. As the potential wells created by

the two kinds of impurity are very different (Fig. 3), we believe this agreement to be accidental. As a matter of fact, it is not observed in the case of the C(7,0) tube we study below.

[32] The potential evolution is very similar for the two p_z orbitals in the DZ basis (see Fig. 3).

[33] For an analytic and numerical study of model Coulomb scattering, see A. G. Petrov and S. V. Rotkin, Phys. Rev. B **70**, 035408 (2004).

[34] Care must be taken with the size of the central device since a too small distance between the defect and the electrodes will result in a significant reduction of transmission in the first energy plateau below the gap.

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[37] The localization radius of the less-bound impurity states just below the vHs has been estimated to ~200 Å in the case of substitutional doping.[15] Taking this value as a lower bound in the K case, the large spatial overlap of the neighboring impurity states starts to slightly enhance the conductance just below the vHs. This effect more clearly develops at higher K concentration (not shown here). One notes, however, that the overestimation of the conductance exactly at the onsets of new subbands is due to computational limitations (see Ref. 36).

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