Supplemental Materials: Electron Confinement Induced by Diluted Hydrogen-like Ad-atoms in Graphene Ribbons

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SI Calculation of Conductance

We include the technical details concerning to the calculation of the LDOS and the two terminal conductance using the Landauer formula and the surface Green's function matching formalism.[1–3] This method divides the system in three blocks. There are two semi-infinite leads made of AGNR, left L and right R described with H_L and H_R Hamiltonian respectively. The finite central part is described by the Hamiltonian matrix H_C, which includes the two doped regions and the separation between them, as depicted in Fig. 1. Thus, the total Hamiltonian is given by:

$$H = H_C + H_R + H_L + V_{LC} + V_{RC}, \tag{S1}$$

where V_{LC}, V_{RC} are the coupling matrix of the left L and right R leads with the central region. The main objective in the method is to calculate the Green's function, which can be written as:

$$G_C(E) = (E\hat{I} - H_C - \Sigma_L - \Sigma_R)^{-1}, \tag{S2}$$

where $\hat{I}$ is the identity matrix, $\Sigma_\ell = V_{\ell C}\, g_\ell\, V^\dagger_{\ell C}$ is the self-energy of each lead $\ell = L,R$, and $g_\ell = (E - H_\ell)^{-1}$ is the renormalized Green's function of the semi-infinite lead $\ell = L,R$. In the linear response regime, the conductance G is calculated as a function of the Fermi energy E, within the Landauer formalism. In terms of the Green's function for the system,[1,2] G reads:

$$G(E) = \frac{2e^2}{h} T(E) = \frac{2e^2}{h} \mathrm{Tr}\left[\Gamma_L G_C \Gamma_R G_C^\dagger\right], \tag{S3}$$

where $T(E)$ is the transmission function across the conductor, and $\Gamma_\ell = i[\Sigma_\ell - \Sigma_\ell^\dagger]$ is the coupling between the conductor and the leads.

Finally, within the Green's functions formalism, the LDOS per atom is proportional to a Green's function matrix element,[4] in a particular the LDOS at the atomic position j, can be expressed as $\mathscr{D}_j(E) = -\frac{1}{\pi}\mathrm{Im}\, G_C^{j,j}(E)$, in such a way that the system LDOS is calculated by $\mathscr{D}(E) = -\frac{1}{\pi}\mathrm{Tr}\,[\mathrm{Im}\, G_C(E)] = \sum_{\text{all atoms}} \mathscr{D}_j(E)$.

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SII Spatial Distribution of Localized and Resonant States

We present the spatial distribution of the LDOS per atom where the red / blue color indicates different sublattice, for the lower sharp states belonging to the metallic band of the ribbon, labeled by (a-d) in the bottom panel of Fig. S1. The bar color scale represents the density probability per sublattice. It is possible to observe some general behavior for these states. First, there is an odd sequence of nodes along the longitudinal

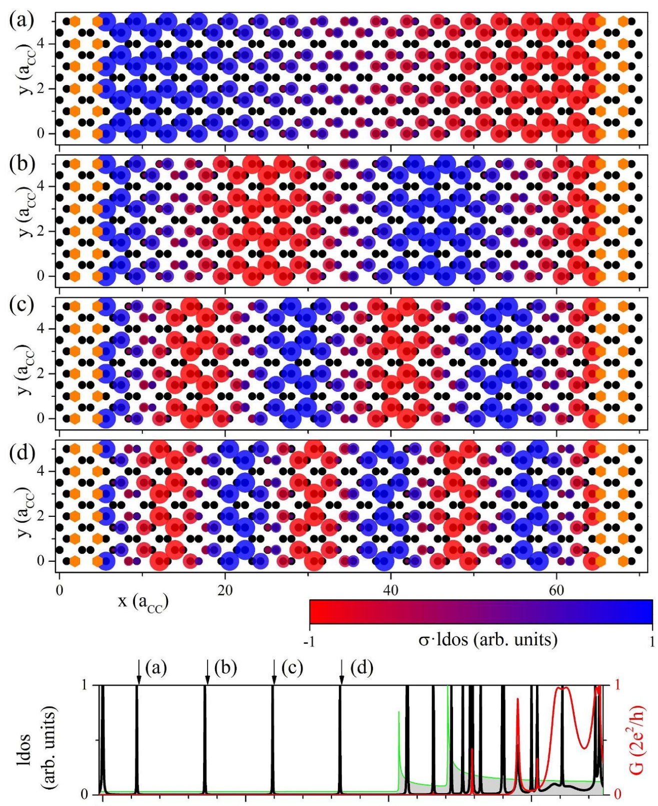

Fig. S1 (Color online) LDOS per atom, red and blue colors represent the sublattice of the atom. The bottom panel shows the LDOS (black line) and the conductance (red line) for a D2-configuration on a metallic AGNR $N = 11$ separated by $L = 15$. The arrows label the energies of the LDOS peaks plotted in the panels (a-d).

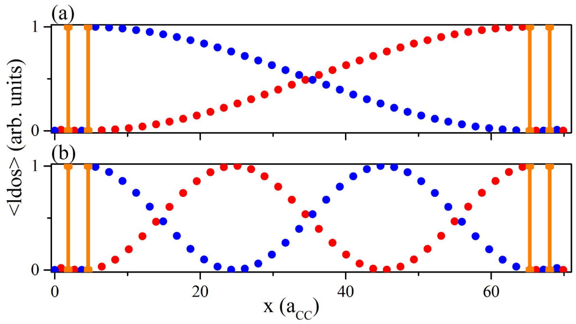

Fig. S2 (Color online) Normalized average LDOS per column of atoms as a function of the x-position for the first two quantized k_x^n-values; (a) $n = 1$ at $E = 0.048\ \gamma_0$ and (b) $n = 2$ at $E = 0.14\ \gamma_0$. Red and blue colors indicate the sublattice, and the orange lines indicate the position of the hydrogen atoms on the ribbon.

ribbon direction, defined by the allowed k_x^n-values. Second, the boundary conditions imposed by the impurities determine the spatial distribution of the LDOS for each sublattice, which exhibits the same feature of standing waves in a pipe with an open ends. This kind of behavior is similar to the observed in edge states of zigzag ribbons. To emphasizes these LDOS features, in Fig. S2 shows the normalized average LDOS per column of atoms (y-direction) as a function of the x-position for the first two quantized k_x^n-values over the envelope metallic band (corresponding to panels (a) and (b) of Fig. S1).

Figure S3 shows the spatial distribution of the LDOS per atom corresponding to the energy states labeled by (a-d) at the bottom panel of the figure. The (a) panel shows the mid-gap state located at zero energy, present in all ordered configurations, regardless if the ribbon is metallic or semiconductor.[5–7] This impurity induced state is highly localized in the nearest-neighbors sites to the adsorbed hydrogen atoms.

The (b) panel shows a non-conductive interface state, which is determined by the band-folding in the k_y-direction. This state corresponds to the first allowed discrete wavenumber, which is below the continuum of the graphene, and consequently, has a higher lifetime. This state is distributed between the hydrogen ad-atoms inside the doped regions.

In panels (c) and (d) show two resonant and extended states, determined by the band-folding in the k_y-direction, which are hybridized with the continuum of the graphene, shown in Fig. 4. The main feature of these states is that they are spread in a narrow energy window, so any electron from the leads injected at these energies easily passes across the system.[8,9]

SIII Comparison with Density-Functional-Theory Calculations

The DFT calculations are performed within the superlattice approach using the density functional based tight-binding method implemented by the DFTB+ code[10] with the associated Slater-Koster parameters.[11] DFTB+ provides an efficient quantum simulation tool based in DFT, which allows us to calculate, in affordable times, the electronic properties of a system with the same size as calculated within a tight-binding approach. Self-consistent charge calculations are converged up to a tolerance of 10^{-8} e for the unit cell similar to the one shown in Fig S4. Ribbons are repeated periodically using super-cell approximation and are separated by an empty space of 10 Å in the perpendicular directions. This cell is large enough to converge results with a single Γ-point. All atoms are relaxed within the conjugate gradient method until forces have been converged with a tolerance of 10^{-3} eV/Å. We check that the relaxed geometry of a single hydrogen atom adsorbed on graphene reproduces well-known results.[12–15] In

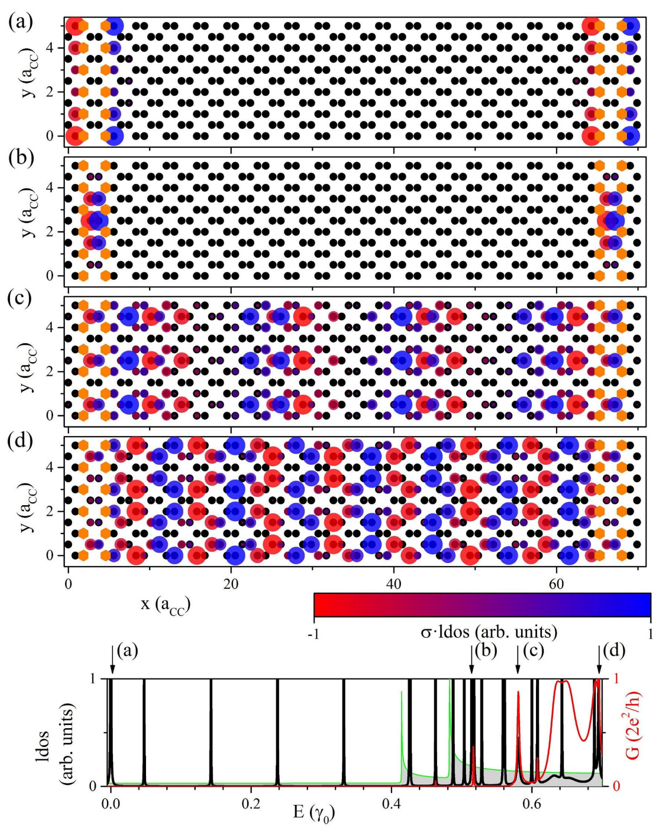

Fig. S3 (Color online) LDOS per atom of: (a) the zero-energy state and (b-d) the interface states at high energies, for the same ribbon parameters of Fig. S1. Red and blue colors indicate the two graphene sublattices.

agreement with these previous works, we found that the hydrogen atoms bonded to carbon atoms are about 1 Å over the graphene plane and its distance to nearest neighbor carbons is about 0.08 Å.

In Fig. S4 we show the isosurfaces of the second harmonic-like state calculated by using the tight-binding and the DFTB+ approach. The latter includes the geometrical corrugation induced by the sp^2 to sp^3 bonds of carbon atoms attached to hydrogen. These states, calculated by two methods, have similar spatial distribution. In panel (a) we have plotted the spatial distribution of the LDOS per atom at $E = \pm 0.46\ \gamma_0 \sim \pm 1.2$ eV obtained by the tight-binding method. As a comparison in Fig. S4 (c) and (d), we have plotted the spatial distribution of the corresponding wavefunction (at energies $E = 1.15$ eV and $E = -1.18$ eV) obtained by using DFTB+ calculations. To facilitate the comparison, atoms have been colored in black and red according the corresponding sublattice. It is important to mention that the energies of the latter states do not preserve the electron-hole symmetry due to the electronic correlation effects; however, they still have a good agreement with the ones previously obtained in the tight-binding model.

Additionally, in the panels (c) and (d), a change in the sign of the wavefunction is evidenced around of the nodes. The wavefunction in (c) is even, while in (d) it is odd. The sign of resonant DFTB+ wavefunctions changes from bonding-like to antibonding-like character for negative and positive energies from E_f, respectively. This parity change means that optical elements between both resonances will be certainly far from zero, and optical transitions between pairs of states could be also detected in experiments.

The wave-functions arising from parabolic bands remind standing-waves on a rope, where both sublattices exhibit nodes at both ends, as shown in Fig. S4(b). This spatial distribution is different from the wave-function originated in the linear envelope-band of Fig. S2, where each sublattice presents a node at one end and a maximum in the other.

Finally, in DFTB+ calculations we look at the energy separation between resonant states. To the separation, we associate an effective energy scaling γ_{eff}, taking in to account the resonant levels far from the Fermi energy. We obtain a value of $\gamma_{\text{eff}} = 2.57$ eV, in good an agreement with the one used through this work.

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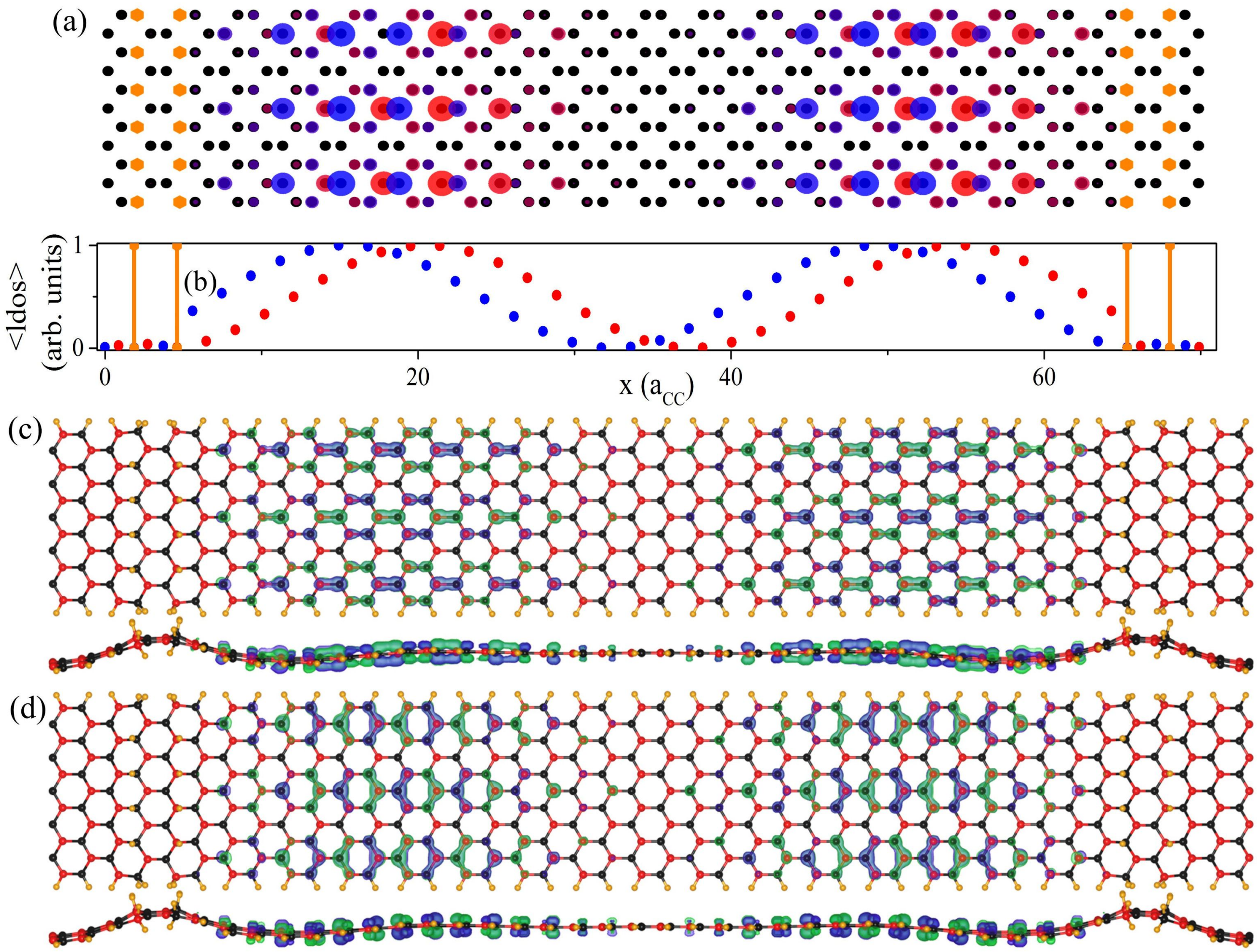

Fig. S4 (Color online) Comparison between the LDOS per atom (red and blue colors represent the sublattice of the atom) calculated within the tight-binding model and the wavefunction at Γ-point calculated within the DFTB+ for a parabolic-band state. The (a) panel shows LDOS by the tight-binding model at $E = \pm 0.46\ \gamma_0 \sim 1,2$ eV, and in panel (b) the averaged LDOS over the *y*-axis as function of the *x*-position. Red and blue colors indicate each graphene sublattice. The equivalent DFTB+ wave-functions correspond to $E = 1.15$ eV and $E = -1.18$ eV in panel (c) and (d), respectively.