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Charge carrier transport and separation in pristine and nitrogen-doped graphene nanowiggle heterostructures

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ABSTRACT

Electronic structure methods are combined into a multiscale framework to investigate the electronic transport properties of recently synthesized pristine and nitrogen-doped graphene nanowiggles and their heterojunctions deposited on a substrate. Real-space Kubo-Greenwood transport calculations reveal that charge carrier mobilities reach values up to 1000 cm^2 V^{-1} s^{-1} as long as the amount of substrate impurities is sufficiently low. Owing to their type-II band alignment, atomically precise heterostructures between pristine and N-doped graphene nanowiggles are predicted to be excellent candidates for charge carrier separation devices with potential in photoelectric and photocatalytic water splitting applications.

1. Introduction

Charge carrier mobility is a key parameter in the performance of electronic devices. In that respect, *sp*^{2} carbon-based materials are known for their exceptionally high promises. Intercalated graphite, carbon nanotubes and mono-, or few-, layer graphene are only a few selected examples in the broad family of *sp*^{2} carbon-based structures [1,2]. One major problem with the deployment of *sp*^{2} carbon nanostructures into practical devices is the lack of control of their semiconducting properties, including their electronic band gap. For instance, carbon nanotubes come in a variety of chiralities and can be either semimetallic or semiconducting, with an electronic gap inversely proportional to their diameter [3]. However, despite recent efforts [4], it remains extremely challenging to grow, or to select after growth, a sharp distribution of carbon nanotube types. Furthermore, graphene is semimetallic and the absence of a band gap is a serious drawback for the development of graphene-based logic devices with switching capabilities. These difficulties highlight the importance of selecting graphene-derived materials displaying a practical electronic band gap.

One possible route to resolve this conundrum is to control spatial confinement to the electronic degrees of freedom by reducing the dimensionality from 2D graphene sheets into 1D graphene nanoribbons [5]. However, electronic transport properties of 1D systems are known to be extremely sensitive to disorder, as stated notably by the theory of localization [6]. Care must therefore be taken since there would be no gain in opening a band gap if mobilities were dramatically affected at the same time. Therefore, the constriction of graphene into 1D ribbons requires to carefully maintain a high structural quality.

In this context, a notable breakthrough has been achieved with the development of bottom-up chemistry approaches, where perfectly edged graphene nanoribbons are obtained from the assembly of small monomers [7–11]. The monomers are gradually assembled by chemical reaction and thermal treatment to first form polymers on a metallic surface by Ullmann coupling followed by cyclo-dehydrogenation to yield the coveted atomically sharp graphene ribbons. The method has shown promising versatility since monomers of various shapes, sizes and compositions can be employed to produce different types of ribbons [7,12,13]. These include graphene nanowiggles, which are ribbons with chevron-like edges [14]. The possibility of assembling larger molecules into wider nanoribbons has also been demonstrated, allowing for a fine tuning of the band gap with the change of the nanoribbon width [9,10,13]. The particular case of graphene nanowiggles has been thoroughly investigated to unveil an unprecedented richness of electronic, magnetic, and thermal properties depending on the combination of edge types [14–17].

In addition to pure hydrocarbon monomers, monomers where a

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number of carbon atoms are substituted by chemical elements such as B or N can also be employed to create atomically precise doped nanoribbons. For instance, nitrogen substitution in the tetraphenyl-triphenylene monomers leads to the fabrication of N-doped graphene nanowiggles [18–20]. Such a doping scheme offers opportunities toward an atomic-level control of dopant positions and concentrations in 1D sp^2 carbon materials. A perfect knowledge of the nitrogen dopant positions in the graphene sublattice is expected to yield a number of well-defined features in the materials' electronic spectrum [21–25]. Moreover, a recent work by Cai et al. [20] showed that pristine and substituted monomers can be used concurrently to produce one of the first atomically-sharp carbon-based heterojunctions.

In this work we focus on the intrinsic properties of the type of heterostructures developed by Cai et al., in 2014. We specifically investigate the electronic properties of pristine and N-doped armchair–armchair (AA-) graphene nanowiggles (GNWs) and their heterojunctions using a combination of density functional theory (DFT) and semi-empirical tight-binding (TB) techniques. We first develop a reliable TB parametrization of the pristine and doped GNWs based on the DFT results to study the electronic transport in two types of GNW heterostructures at micrometer scale. Such size upscaling is made possible within the real-space Kubo-Greenwood formalism. The first system under consideration consists of a pristine GNW with random inclusions of N-doped GNW segments. The second system is a long GNW with a single sharp junction between a pristine and a N-doped region deposited on a substrate containing charge impurities. Finally, the potential of such heterostructured GNWs for charge separation devices in particular for photocatalytic water splitting and photoelectric application is discussed.

2. Electronic structure of pristine and N-doped AA-GNWs

2.1. First principles calculations

Density functional theory (DFT), as implemented in SIESTA [26] and VASP [27,28] packages (see Method section for computational details), was employed to compute the electronic band structures and density of states (DOS) of the pristine and nitrogen-doped AA-GNWs. The selected systems correspond to those that were recently experimentally realized [18–20]. Let us first introduce the notation adopted here for the doping scheme: a monomer where n carbon atoms are substituted with n nitrogen atoms is labeled Nn monomer, and the corresponding assembled GNW is likewise denoted as Nn GNW [25], as shown in Fig. 1. Only the results based on the SIESTA package are presented in Fig. 1 (d–f) (black thick lines), since a good agreement for the electronic structures was obtained with both DFT codes.

As shown by the computed electronic band structure diagrams (Fig. 1(d–f) left panels), the three systems have a direct band gap of similar size, i.e., 1.610, 1.613, and 1.540 eV for the pristine, N2 and N4 GNWs respectively. It is important to note that DFT typically underestimates fundamental band gap values. More sophisticated treatments, such as the use of many-body *GW* approach for quasi-particle correction and the image charge model for substrate polarization-induced gap reduction, provide fundamental band gap values in the 2.0–2.8 eV range [25,29–32], in much better agreement with experiments. Note that different experimental works reported different fundamental gap values: some reported ~2.8–3.1 eV [10,18] while others measured ~2.0 eV gaps [20,33]. The origins of these discrepancies can partially be traced back to substrate polarization effects. Although the band gaps are underestimated by DFT, a scissor-type correction can be applied to the presented results without modifying the conclusions on transport properties since the dispersion and overall shape are not significantly affected by the underestimated band gap [34,35]. Overall, the band structure of the AA-GNWs are characterized by pairs of electronic bands separated by small gaps. Interestingly, the pristine and N2 GNWs have almost exactly the same electronic structure, especially for the first two pairs of valence and conduction bands located within the −1.5–1.5 eV energy window. A more pronounced difference appears for the third group of valence and conduction bands. However, as indicated by blue arrows in Fig. 1(e), a clear distinction between these two systems is the presence of two pairs of superimposed flat bands at energies −1.57 eV and −1.66 eV in the case of the N2 GNW. These flat bands correspond to the lone electron pairs localized at the non-hydrogenated nitrogen edge atoms (blue atoms in Fig. 1(b)). These lone electron pairs are strongly localized, as further shown by the non-dispersive character of the corresponding bands. In addition, these electrons do not interact significantly with the rest of the electronic structure and are therefore not appreciably hybridized with the π electronic cloud. This feature is even more pronounced in the N4 GNW system (see Fig. 1(f)), for which these flat bands lie at an energy (−1.30 eV) where dispersive π valence bands are present, without being hybridized. Apart from the position in energy of these flat bands, the main difference between N2 and N4 GNW electronic band structures is observed at about 4/5 of the $\Gamma - X$ line. Around this k point the first two pairs of valence (conduction) bands join (repeal) each others in the case of N4 GNW. The density of states (DOS) corresponding to these band structures is displayed in the central panels of Fig. 1(d–f). A series of van Hove singularities are obtained at the band edges, as expected for 1D systems. Another set of sharp peaks are also observed for energies corresponding to the isolated lone pairs of electrons in case of the N2 and N4 GNWs.

2.2. Parameterized tight-binding calculations

In order to study mesoscopic-sized systems, we developed a single-band tight-binding (TB) model that reproduces the DFT electronic structure of the three types of AA-GNWs mentioned above (See Method section for details). The corresponding TB band structures and DOS are plotted in thin red lines on top of the DFT results in Fig. 1(d–f). An overall good agreement is obtained between TB and DFT electronic structure, in particular for the first two pairs of valence and conduction bands. We also note that depending on the system, the third group of valence and conduction bands is not always accurately reproduced. This is not surprising since our single-band tight-binding model is not expected to represent states that have a significant *s* character. In spite of this, it is justified to use a TB model that accurately represents the properties in an energy windows of ±1 eV since we focus on relatively low-energy transport properties around the top of valence and bottom of conduction bands. This is justified by the fact that in actual transport experiments, the gate voltages (and gate capacitance) hardly allow electrons and holes to reach energies outside a window of ±1 eV with respect to the Fermi level. Therefore in the present case, the transport properties will be dominated by the two first groups of valence and conduction bands. The flat bands corresponding to the lone pairs of electrons ascribed to the nitrogen atoms, are not reproduced by the TB model (Fig. 1(e–f)), since the TB model only accounts for π electrons. However, as discussed earlier, these electronic states do not mix with other electronic states and do not contribute to charge transport since they have a vanishing group velocity.

3. Electronic structure of AA-GNW heterostructures

It has been experimentally shown possible to mix monomers with different compositions to fabricate long GNWs containing