Electron and Optical Spectroscopies of Graphene Nanoribbons: Insights from Ab-Initio Calculations

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Graphene nanostructures have striking properties related to the lateral confinement that can open a band gap and induce semiconducting behavior with controlled quantum states and a variety of peculiar width- and edge-related phenomena depending on the details of the atomic structure. Radically new functionalities can thus be designed, far beyond those expected from extended graphene systems or conventional semiconductors.

Key features connected to the tunability of electronic and optical properties as a function of structural parameters, e.g. width and edge structure of graphene nanoribbons (GNR), have been predicted theoretically (see e.g. [1-2]); however, only recently atomic control of GNR geometry (orientation, width and edge termination) was demonstrated by a novel approach based on depositing molecular precursors on appropriate substrates, which catalyze polymerization and ribbon formation [3]. These advancements in the fabrication procedure have thus allowed the first measurements (Fig. 1) of the band gap and the topology of the occupied bands of atomically precise armchair GNRs (AGNR's) by scanning tunneling spectroscopy (STS) and angle-resolved photoelectron spectroscopy (ARPES) techniques [4,5].

In this work we combine cutting edge theoretical and experimental techniques to study the electronic structure of a specific armchair nanoribbon (N=7, 7-AGNR). In particular we compare many-body perturbation theory calculations (performed at the GW level) with ARPES and STS data.

First principles calculations based on Density Functional Theory (DFT) were carried out for 7-AGNR, both isolated and on Au(111) substrate. Calculations were performed within the local-density approximation (LDA) for the exchange-correlation potential, using a plane-wave basis set and pseudopotentials. We carefully checked the effect of van der Waals corrections. We find a graphene/Au distance of 3.31 Å and a negligible electronic interaction (i.e. band hybridization), in excellent agreement with existing literature. For the H-passivated 7-AGNR we determine an average C-Au distance of 3.15 Å, and little to negligible band hybridization of the electronic bands of GNRs and Au(111). Our findings clearly show a weak interaction between 7-AGNR and the Au(111) metal substrate. In order to compare ARPES and STS experiments, we have computed the self-energy corrections to the electronic structure by means of many-body perturbation theory, within the so-called GW approximation at the G_0W_0 level. As depicted in Fig. 2 (left-hand side), the GW correction brings the LDA gap from 1.6 to 3.7 ± 0.1 eV [2]. We then estimated the gap reduction due to the presence of the metallic substrate by adding the image charge (IC) correction to the GW energy gap of the isolated GNR (Fig. 2, right-hand side). Overall, this results in a theoretical estimate of the energy band gap of 2.3 to 2.7 eV for the 7-AGNR on Au(111), which is in very good agreement with the experimental value of 2.3 ± 0.1 eV.

The above results show that our ab-initio theoretical scheme can provide quantitative predictions for electron spectroscopies of nanoribbons on weakly coupled substrates such as Au. Recent results for optical excitations and excitonic effects will also be discussed, including the spectral evolution from molecular and polymer precursors to nanoribbons.

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Figures

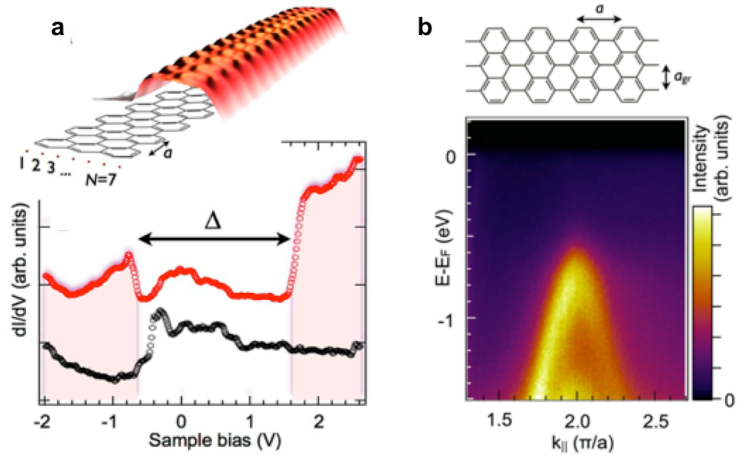

Figure.1: (a) Scanning tunneling microscopy (STM) image (U = 2.2 V, I = 0.15 nA, 5 K) and chemical structure of an armchair graphene nanoribbon of width N= 7 (7-AGNR) on Au(111) (b) ARPES intensity plot I(E EF,k||) recorded along the ribbon axis revealing the two occupied frontier bands (raw data, hv = 37 eV, T = 300 K). The atomic structure of the H-terminated 7-AGNR is reported for clarity.

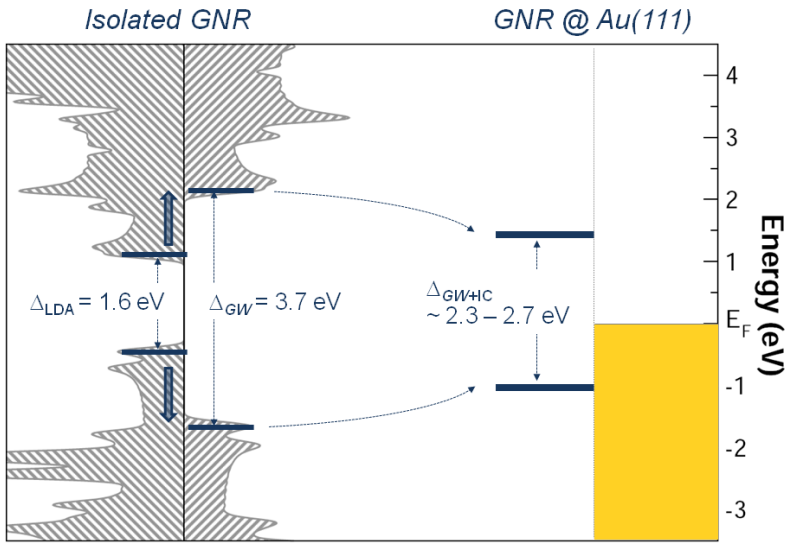

Figure 2: LDA and GW-corrected DOS (energy gap highlighted) for the gas phase 7-AGNR are shown on the left side. By taking into account the surface screening, the gap is reduced to 2.3 - 2.7 eV, as shown on the right side. The molecule-Au(111) distance has been estimated to be 3.15 Å.