Origin of Rectangular-like Lattice on Nanographene in STM Images Unveiled by First-principles Calculations

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We performed atomic-scale scanning tunneling microscopy (STM) of a cleaved highly oriented pyrolytic graphite [1]. Together with a $(\sqrt{3} \times \sqrt{3})R30°$ phase (Fig. 1(c)), a unique rectangular-like lattice (Fig. 1(d)) was resolved on a graphene nanosheet at a sample bias (V_s) of -0.05 V. To clarify the origin of this rectangular lattice, we conducted first-principles calculations [2] based on density functional theory and obtained simulated STM images of armchair-edged graphene nanoribbons (AGNRs) with different widths. In terms of the ribbon width (Fig. 2(a)), W is defined as the number of dimer lines across the ribbon width [3]. To avoid inaccuracies in the Fermi level, we used the sum of the electron density of orbitals in $[\varepsilon_{\mathrm{HOMO}} + eV_s,\ \varepsilon_{\mathrm{HOMO}}]$ for a negative sample bias, where $\varepsilon_{\mathrm{HOMO}}$ indicates the energy level of the highest occupied molecular orbitals (HOMO). The band structure was magnified in Fig. 2(c). V_1 and V_2 denote different energy levels at $k = 0$. Fig. 2(d) shows simulated STM images at both sample bias of V_1 and V_2. At the lower sample bias (V_1), we find a rectangular superstructure similar to our experimental results [1]. The other image at V_2 indicates the ring-like shapes within the AGNR, which is in good agreement with the hexagonal lattice of graphene.

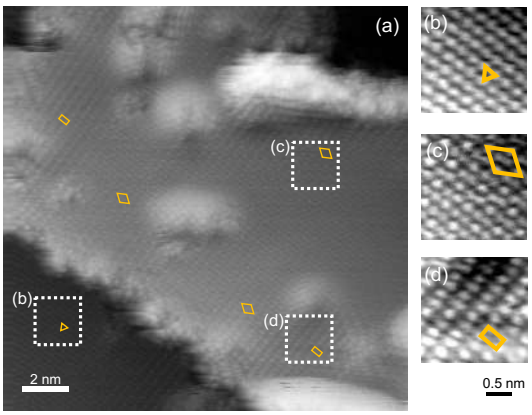

Figure 1. STM images of a small graphene sheet on graphite.

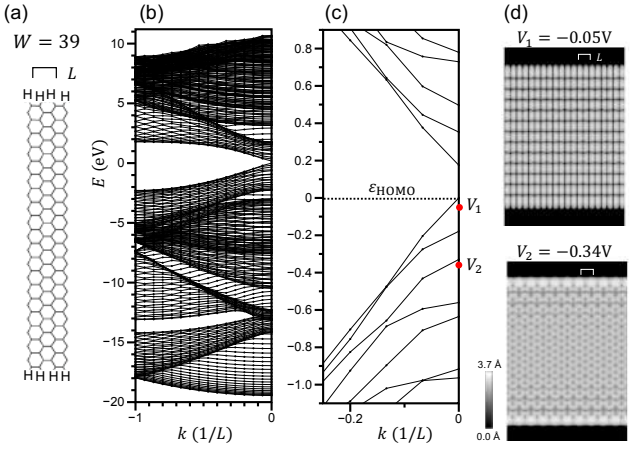

Figure 2. The band structure and simulated STM images of an AGNR with $W = 39$.

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Supplementary information:

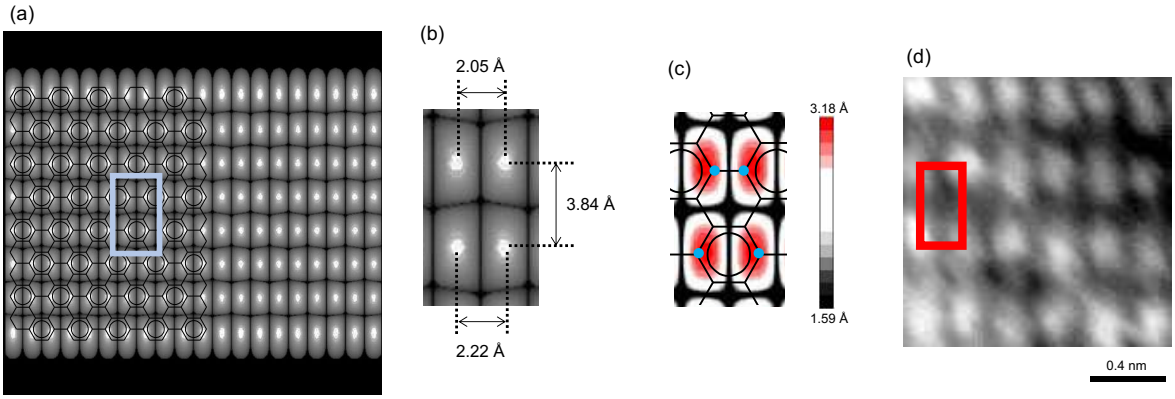

Figure 3. (a) Simulated STM image of an AGNR with $W = 24$ at a sample bias of -0.05 V. The Clar representation is partially superimposed. (b) The area indicated by the solid line-box in (a). The distances between the bright spots are indicated with arrows. In (a) and (b), a nonlinear gray scale is used to highlight the highest sites at each vertex of the rectangular lattice. (c) The area in (b) is depicted using a linear colored scale with the corresponding Clar formula. Filled (blue) circles represent the positions of the nearest carbon atoms from the sites with high density of states. These carbon atoms form a trapezoid whereas the four red ovals are the vertices of the rectangular lattice. (d) The experimental features in Fig. 1(d) agree well with (b) and (c).

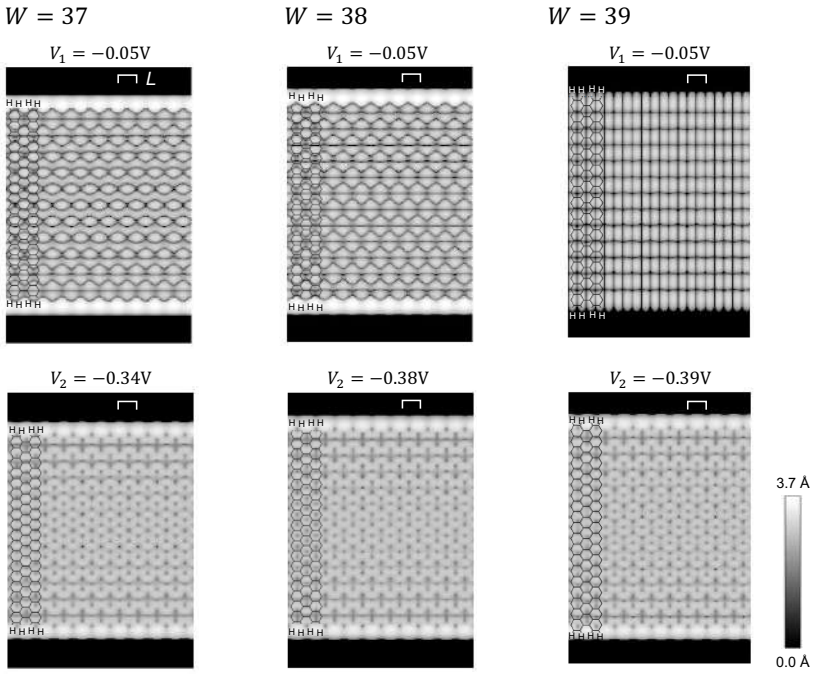

Figure 4. Simulated STM images of AGNRs with three different subclasses as $W = 37$ (left), $W = 38$ (center), and $W = 39$ (right). The ribbon configurations were superimposed in each image, and the sample bias to obtain the images was provided.