Supplementary section for *ab initio* simulation

The exchange-correlation potential employed was the one parameterized by Perdew and Zunger [S1] based on the Ceperley-Alder data [S2]. Core electrons were replaced by norm-conserving Troullier-Martins pseudopotentials [S3]. Pseudopotentials and numerical atomic orbital basis have been employed before [S4–S6]. We used double-ζ plus polarization numerical atomic orbitals to expand the electronic wavefunctions, and we employed a mesh cutoff of 220 Ry to compute the overlap integrals. Transmission spectra and current-voltage (I-V) characteristics are investigated by the Nonequilibrium Green's Function (NEGF) approach based on the Density Function Theory (DFT) implemented in the TranSIESTA module (included in the SIESTA package). We chose LDA because it describes the spacing between the graphene and Si(100) better than the generalized gradient approximation functional [S7]. To achieve reasonably accurate results, the LDOS were computed with an 8×8×1 Monkhorst-Pack k-point mesh size [S4, S6]. We use the asymmetric 2×1 dimer reconstruction of the Si(100) surface for calculations involving graphene flakes, graphene nanoriboons (GNRs) and infinite graphene with periodic boundary conditions along the graphene plane. Each graphene flake consists of 3×3 graphene unit cells with all of the edges H-passivated. The graphene flakes and infinite graphene covered Si(100) surfaces are discussed in the main text of the manuscript. Here, for the completeness of the simulation work, ZGNR and AGNR are also presented in Fig. S1 (a) and Fig. S1(b), respectively. To remove the GNR edge effects, we apply periodic boundary conditions. Following previous convention [S6, S8], the GNRs with zigzag shaped edges on both sides are classified by the number of the zigzag chains (Nz) across the ribbon width. Likewise, ribbons with armchair shaped edges on both sides are classified by the number of dimer lines (Na) across

the ribbon width. We refer to a GNR with Nz zigzag chains as an Nz-ZGNR, and a GNR with Na dimer lines as an Na-AGNR. Each zigzag GNR under consideration contains 12 zigzag atomic chains across its width (12-ZGNR) and has 6 units along its length. To commensurate the zigzag GNRs with the 4×4 unit cells of Si(100)-2×1surface structure, we stretch the zigzag GNRs along the y-axis by 3.5%. Each armchair GNR under consideration contains 10 dimers across its width (10-AGNR) and 7 units along its length. To commensurate the armchair GNRs with the 8×4 unit cells of the Si(100)-2×1 surface structure, we stretch the armchair GNRs along the x-axis by 2.4%. To commensurate the infinite graphene with the 8×4 unit cells of the Si(100)-2×1 surface structure, we stretch the infinite graphene along the x-axis by 2.4% and the y-axis by 3.5%, respectively. In all cases, a slab of five silicon monolayers with a height of 5.44 Å is employed. The bottommost layers are H-passivated. The graphene monolayers are placed in proximity to the uppermost silicon layers. To remove the dangling bonds of the silicon substrates, periodic boundary conditions are applied to the substrate. The vacuum region in the vertical direction is at least 10 Å in order to provide enough separation between periodic images.

To obtain the optimally stable configuration of the combined system, the initial spacing between the graphene layer and the topmost layer of the Si surface was chosen to be 2.5 Å for both Si(100):H and clean Si(100) geometrical relaxing, which is the typical van der Waals interaction distance. The experimental measurement shown in Fig. 1(d) of the manuscript also indicates that this initial spacing is a reasonable starting point for *ab initio* simulation. We allowed all the atoms to move and search energy-stable positions except the bottom silicon and hydrogen layer by a conjugate-gradient method. After full geometry optimization and relaxation, no covalent bonding between C and Si atoms is found near the Si (100)-2×1:H surface shown in Fig. S2(a, c). For the clean Si(100)-2×1 surface case, the graphene sheets are attached to the

dangling Si surface atoms, and surface-graphene Si-C σ bonds are formed shown in Fig. S2(b, d).

We also investigate adsorption energies of the graphene monolayers on the Si(100) surfaces. The adsorption energies ($E_{adsorption}$) are calculated by the energy difference between the total energies of the combined system and the sum of the total energies of the isolated graphene and the Si(100) substrate, that is, $E_{adsorption} = E_{total}$(separate system) − E_{total}(combined system). The comparison of adsorption energy of various graphene and Si substrates is shown in Table 1. The adsorption energy of graphene on an H-passivated surface is lower than that on an unpassivated surface, as there are no dangling bonds on the H-passivated silicon surface and no additional new bonds formed during the adsorption process. The large adsorption energies demonstrate that graphene on the clean Si(100) surfaces are energetically stable.

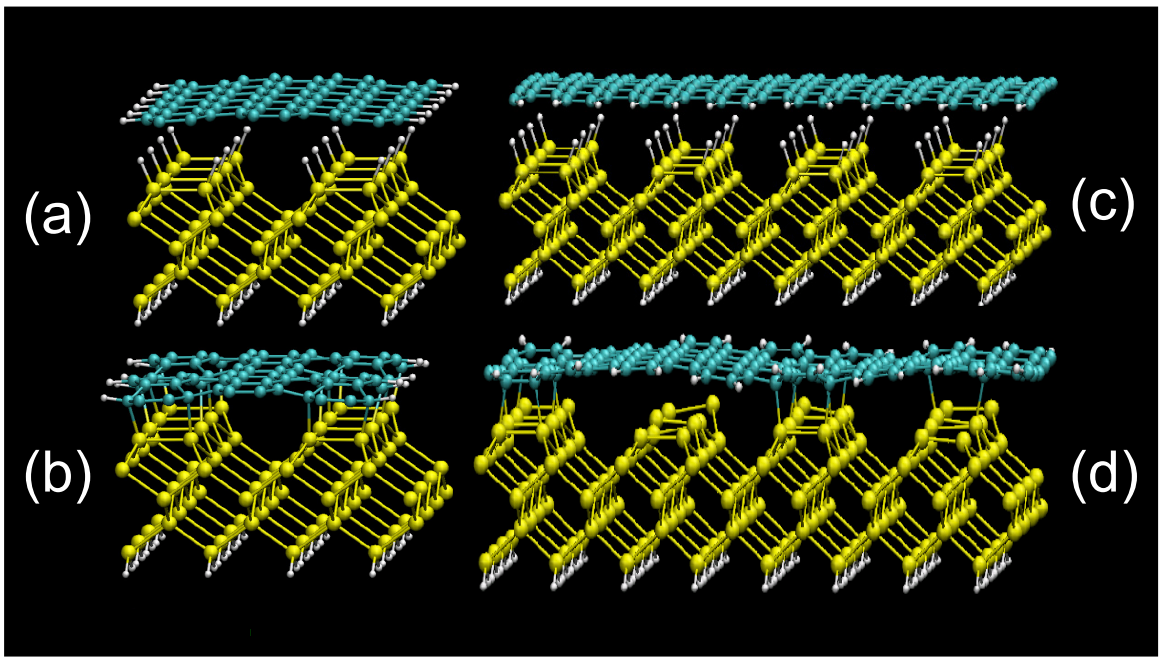

FIG. S1: Geometries of the graphene adsorbed on silicon surfaces. The structures are fully relaxed with residual forces less than 0.01 eV/Å. The vacuum region in the vertical direction is at least 10 Å in order to provide enough separation between periodic images. (a) A 12-ZGNR

adsorbed on the Si(100)-2×1:H surface. (b) A 12-ZGNR adsorbed on the clean Si(100)-2×1 surface. (c) A 10-AGNR adsorbed on the Si(100)-2×1:H surface. (d) A 10-AGNR adsorbed on the clean Si(100)-2×1 surface.

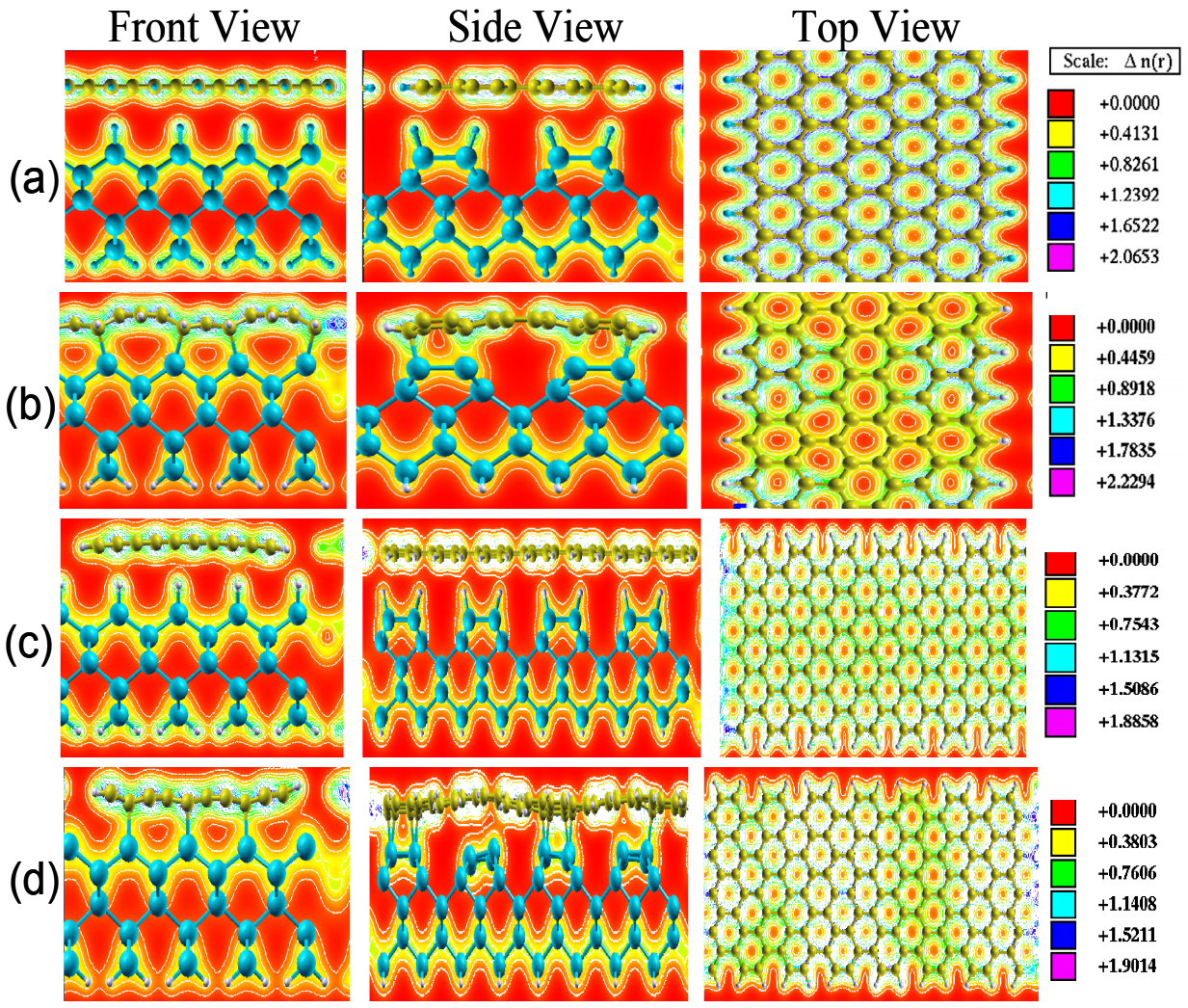

FIG. S2: Charge density contour plots (spacing in electrons per $Å^3$) to visualize the relative interaction between the graphene monolayer and the Si substrate. (a) 12-ZGNR adsorbed on the Si(100)-2×1:H surface. (b) 12-ZGNR adsorbed on the clean Si(100)-2×1 surface. (c) 10-AGNR adsorbed on the Si(100)-2×1:H surface. (d) 10-AGNR adsorbed on the clean Si(100)-2×1 surface. After full geometry optimization and relaxation, no covalent bonding between C and Si atoms is

found near the Si(100)-2×1:H surface. For the clean Si(100)-2×1 surface case, the 12-ZGNR and 10-AGNR are attached to the dangling Si surface atoms, and surface-graphene Si-C σ bonds are formed.

TABLE 1: The adsorption energies of graphene on Si(100) surfaces

Adsorption energies	Si(100)-2×1:H	Clean Si(100)-2×1
Flakes	7.1338 eV	20.5079 eV
12-ZGNR	7.5426 eV	21.2835 eV
Infinite Graphene	8.7604 eV	19.1002 eV
10-AGNR	8.9351 eV	16.2753 eV

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