Supplementary Information (SI) for Journal of Materials Chemistry A.

Supporting Information

Unraveling the Standing-Up Orientation Transition of π-Conjugated Molecules on Graphene Templates

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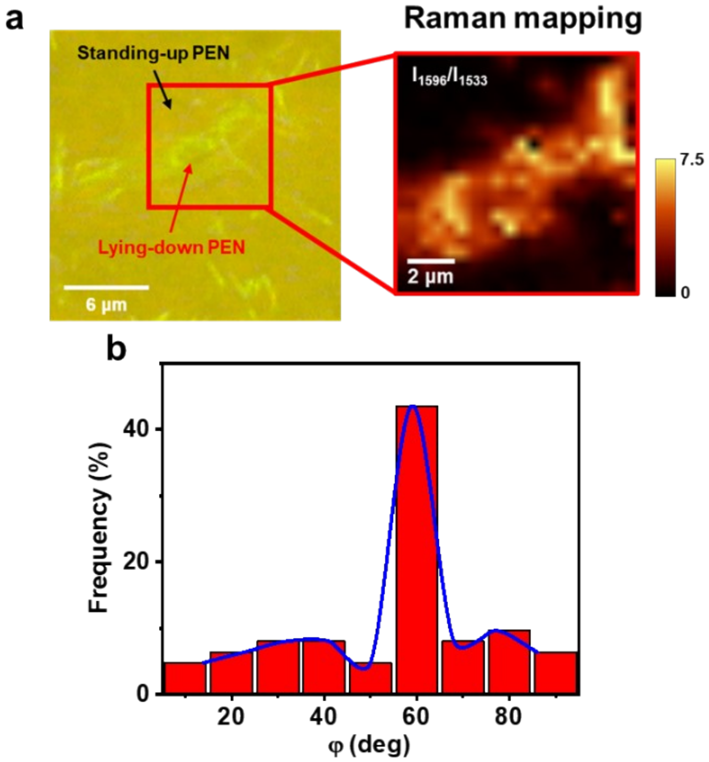

Figure S1. (a) Raman mapping data of pentacene islands deposited on a flat SiO_2 substrate at 75°C. (b) Histograms depicting the distribution of relative angles between rod-like pentacene islands directly formed on the graphene surface for both G/SiO_2 and G/SAM substrates.

Under the same conditions used for the flat G/SiO_2 sample at 75°C, shown in Figure 1, pentacene deposition was performed on the substrate. We used Raman mapping to analyze growth modes at various points during the early growth stage. Previous research has indicated that islands with a lying-down growth mode tend to exhibit a higher I_{1596}/I_{1533} intensity ratio compared to those with a standing-up growth mode. In our Raman mapping, conducted over a 20 μm × 20 μm area, rod-like islands with relatively greater heights consistently displayed a high I_{1596}/I_{1533} intensity ratio of approximately 7. In contrast, platelet-like islands, with lower island thicknesses, exhibited weaker I_{1596} peaks, resulting in a lower ratio of about 0.3. These observations strongly confirm that the lying-down growth mode dominates in rod-like islands, whereas the standing-up growth mode is characteristic of platelet-like islands during the early growth stage.

Figure S1b shows the distribution of relative angles between rod-like islands directly formed on the graphene surface for both G/SiO_2 and G/SAM substrates. The distribution reveals distinct peaks around 60°, which is consistent with the 6-fold rotational symmetry of the graphene lattice. This suggests the epitaxial growth of rod-like islands on the graphene surfaces.[1-2] This observation further supports the dominance of the lying-down growth mode in rod-like islands.

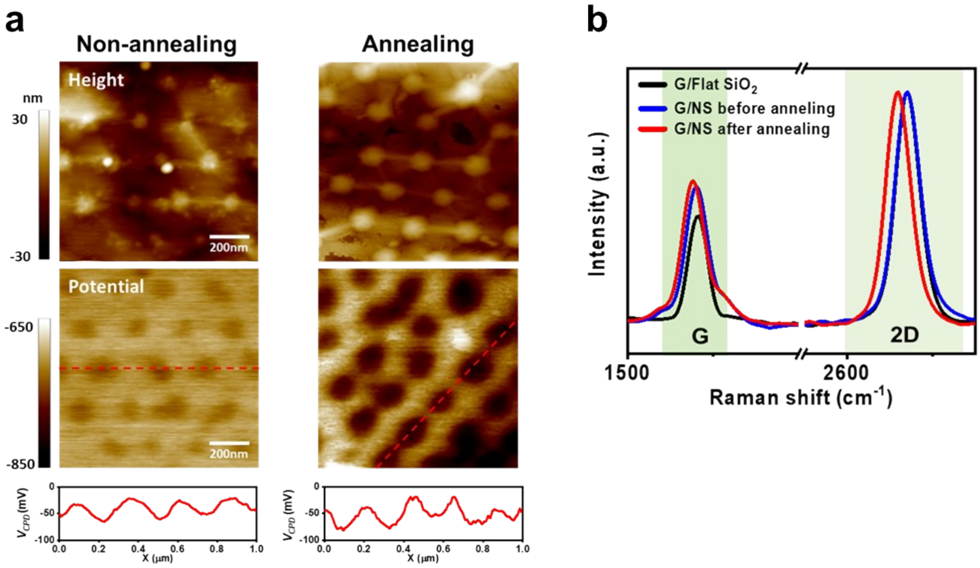

Figure S2. Contact potential difference (V_{cpd}) of G/NS before and after annealing using KPFM (Kelvin Probe Force Microscopy) measurement

To investigate the spatial distribution of strain, we conducted Kelvin probe force microscopy (KPFM) measurements using n-doped Si tips. KPFM determines the local work function of graphene by measuring the contact potential difference (CPD), calculated as $CPD = (\varphi_{tip} - \varphi_{sample})/e$, where φ_{tip} is the work function of the n-doped Si tips (~4.1 eV), φ_{sample} is a work function of graphene, and e represents the elementary charge. In this setup, a more negative CPD indicates a deeper graphene work function. The spatial resolution of KPFM, governed by the AFM tip's cantilever, is comparable to or larger than the diameter of a single silica nanosphere. Thus, the local work function reflects the spatially averaged work function within the surrounding region. Despite this averaging, KPFM measurements qualitatively indicate variations in the local work function of graphene. Given the similar doping levels in both apex and free-standing regions, differences in local work function can be attributed to strain-induced pseudo-electric fields. By comparing the height and CPD images of the G/NS-array (Figure S2a), it becomes clear that the graphene work function is deeper at the apex regions compared to the free-standing regions. The increased difference in work function between the apex and freestanding regions after annealing suggests that, while the strain in the freestanding regions remains nearly zero, the biaxial strain at the apex regions has intensified. It supports the assumption tensile strain concentrated at the apex regions, consistent with earlier simulation results.[1]

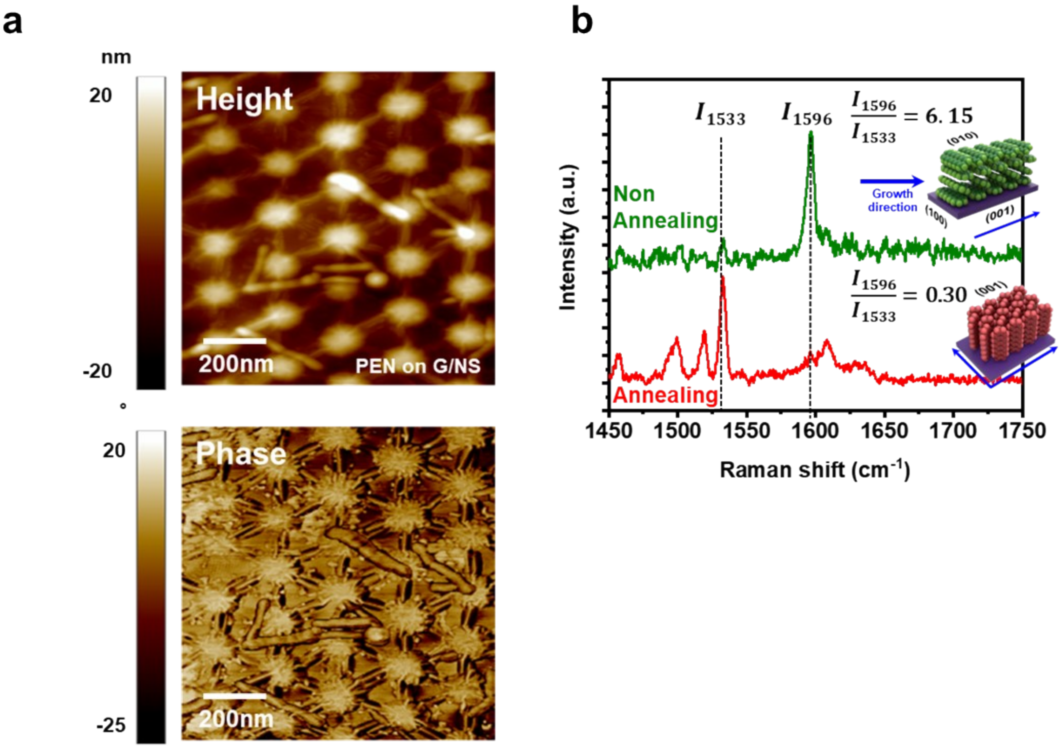

Figure S3. Pentacene deposition on non-annealed G/NS templates

Reference

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