Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information for

Complex three-dimensional graphene structures driven by surface functionalization

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DFT and molecular statics simulations

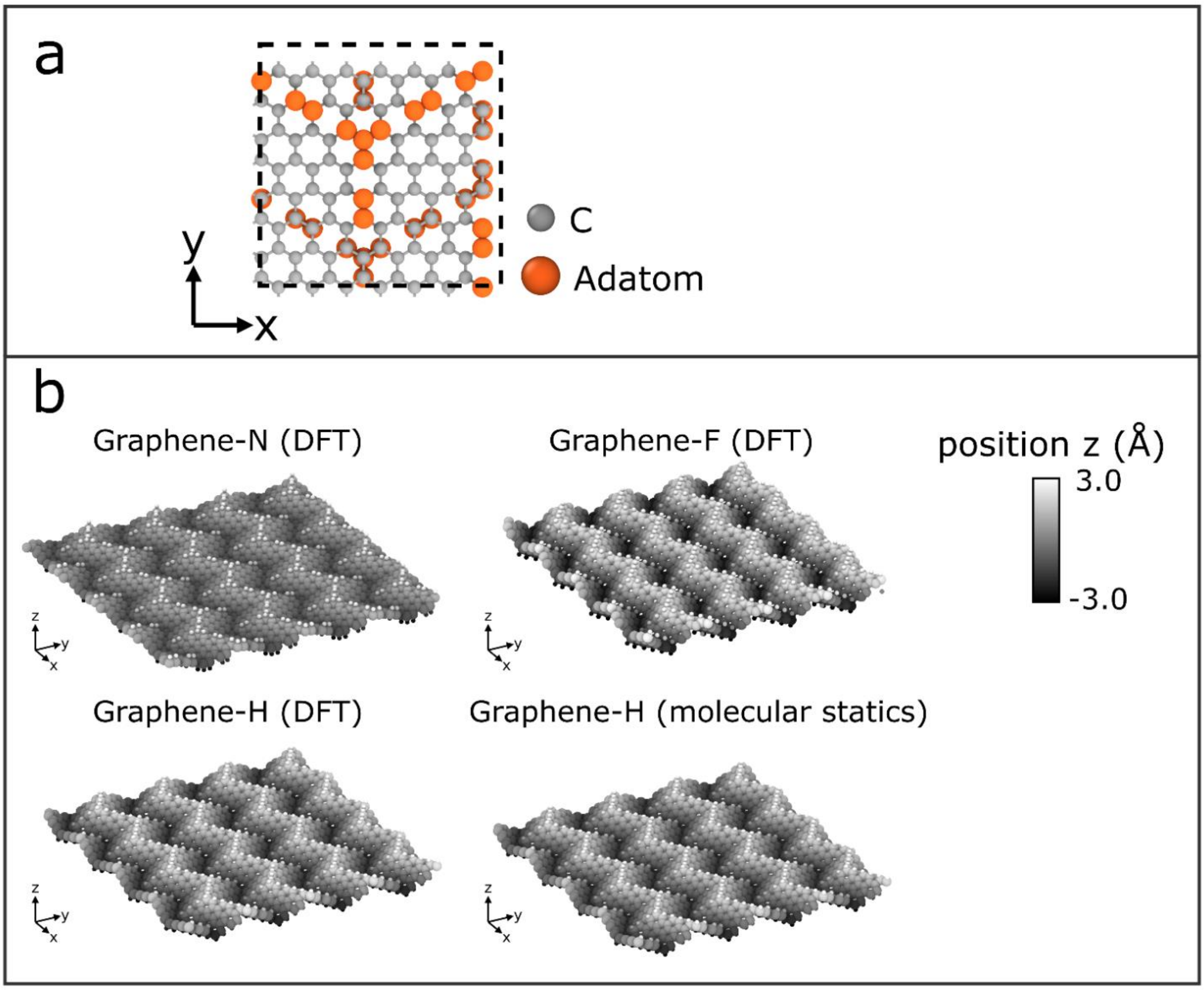

Figure S1: Formation of graphene Miura-ori structures using surface functionalization with different adatom types (4×4 supercell). To save computational resources in the DFT calculations a 1×1 supercell is considered for all cases. a: Initial configuration. b: Final configurations obtained by DFT calculations and molecular statics simulations. Results for different supercell sizes ranging from 1×1 to 4×4 show negligible differences in molecular statics simulations. Similarity between the DFT and molecular statics results implies general validity of the findings.

Folding angle in a 2D material sheet induced by functionalization

To understand the mechanism of the folding in a 2D material sheet induced by functionalization, we focus on a simple pattern with a straight fold of width *w* and infinite length in the *y*-direction, see Figure 2a in the main text. A molecular statics simulation is employed to obtain the relaxed configuration of a graphene sheet induced by hydrogenation with this folding pattern. A periodic boundary condition is applied in the *y*-direction to simulate infinite length (not in the *x*-direction). We consider $w = 8.1$ nm and a density of $\rho = 3\%$. Figure 2a in the main text shows the result of the relaxation. The functionalization leads to a cylindrical deflection with constant radius R across the fold and a folding angle of 79°. We find that the folding angle is a linear function of w and ρ.

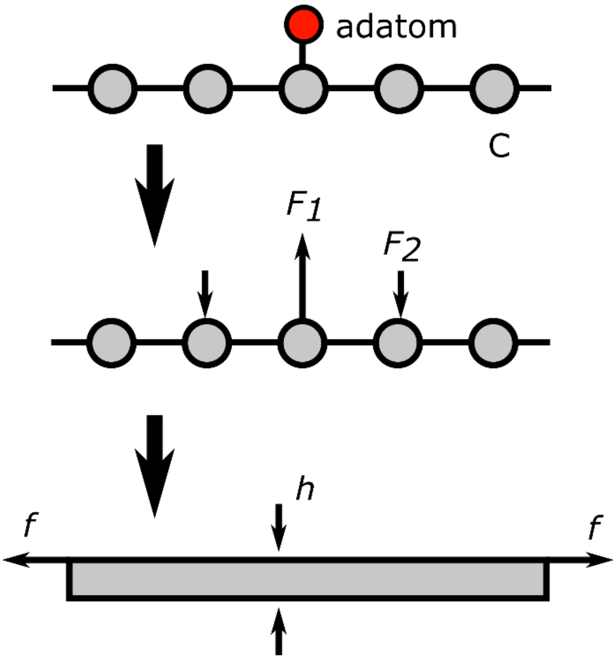

Figure S2: Pseudo surface stress due to surface functionalization. The adatom induces an attractive force F_1 and repulsive forces F_2, causing bending and stretching.

To obtain an analytical formula for the folding angle, we model the 2D material sheet as a thin plate using the classical plate theory (Kirchhoff-Love plate theory) with some modifications. According to Figure 2a in the main text and Figure S2, the pseudo surface stress f (unit: force/length) induced by the functionalization will exert a bending moment density (unit: force) on the thin plate of

$$M = \frac{fh}{2}, \tag{S1}$$

where $h = 3.35$ Å is the effective thickness of graphene. When the ratio w/L_y is sufficiently small, where L_y is the length in the y-direction, the bending moment density will result in a bending of the thin plate across the fold with constant radius R. According to classical plate theory, R fulfils

$$\frac{1}{R} = \frac{M}{D}, \tag{S2}$$

where D is the bending modulus of the thin plate. Substituting Eq. (S1) into Eq. (S2) yields

$$\frac{1}{R} = \frac{fh}{2D}. \tag{S3}$$

Therefore, the folding angle of the 2D material sheet induced by the pseudo surface stress is

$$\theta = \frac{w}{R} = \frac{fhw}{2D}. \tag{S4}$$

We assume (valid as long as ρ does not exceed 50%) that the pseudo surface stress is directly proportional to the density of the adatoms, $f = \rho s$, where s is a material constant describing the pseudo surface stress when the 2D material sheet is fully functionalized. As a result, the folding angle in Eq. (S4) can be rewritten as

$$\theta = \frac{hs}{2D} w\rho. \tag{S5}$$

The calculation of the folding angle by Eq. (S5) requires the determination of s and D, which is discussed below.

The Kirchhoff-Love plate theory in continuum mechanics assumes that stress and strain vary linearly through the thickness of the thin plate. Then, the bending modulus of the 2D material sheet is $D = \frac{Et^3}{12(1-\nu)}$ where E, ν, and t are the Young's modulus, Poisson's ratio, and thickness, respectively. However, for an atomic monolayer the definition of the thickness for the bending is ambiguous [1]. One can determine D without this concern by means of the strain energy density

$W = \frac{1}{2} D\kappa^2$, where $\kappa = \frac{1}{R}$ is the curvature induced by the bending. In practice, W can be obtained by calculating the energy of nanotubes with different radius R [2].

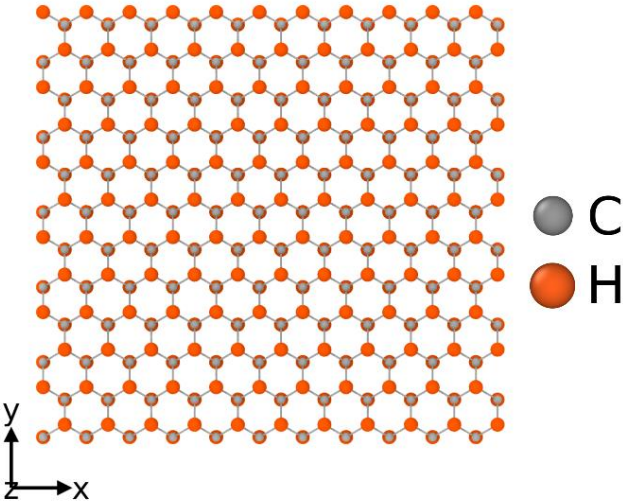

Figure S3: Hydrogenation on top and bottom of a graphene sheet with ρ = 50%.

As the pseudo surface stress is assumed to be directly proportional to ρ, the material constant s is the same as in the case of functionalization of both sides of the graphene sheet with ρ = 50%, as shown in Figure S3. The pseudo surface stresses on the two sides stretch the graphene sheet rather than bending it (as it would be the case for hydrogenation on one side only) because the bending moments on top and bottom cancel each other. The amount of stretching obtained by molecular statics simulation with the REBO-II potential is $\left(\varepsilon_{xx}^{e};\varepsilon_{yy}^{e};\varepsilon_{xy}^{e}\right)=\left(0.029;0.029;0.00\right)$, where the normal strain ε_{xx} (ε_{yy}) is the relative change in length from the pristine to the hydrogenated sheet in the x-direction (y-direction), and the shear strain ε_{xy} describes the change in shape. Consequently, by stretching the pristine structure with the strain $\varepsilon_{ij}^{e}\,(i, j = x, y)$, we can calculate the pseudo surface stress tensor component $s_{ij} = t_0\sigma_{ij}$, where t_0 is the thickness of the pristine sheet and $\sigma_{ij} = \frac{1}{At_0}\frac{\partial E_{tot}}{\partial \varepsilon_{ij}}\Big|_{\varepsilon_{ij} = \varepsilon_{ij}^{e}}$ is the in-plane stress tensor (A being the area and E_{tot} the total energy). We obtain $s_{xx} = s_{yy} = s = 9.7$ N/m and $s_{xy} = 0.0$ N/m. Repetition of the procedure using DFT calculations leads to a value of $s = 10.1$ N/m.

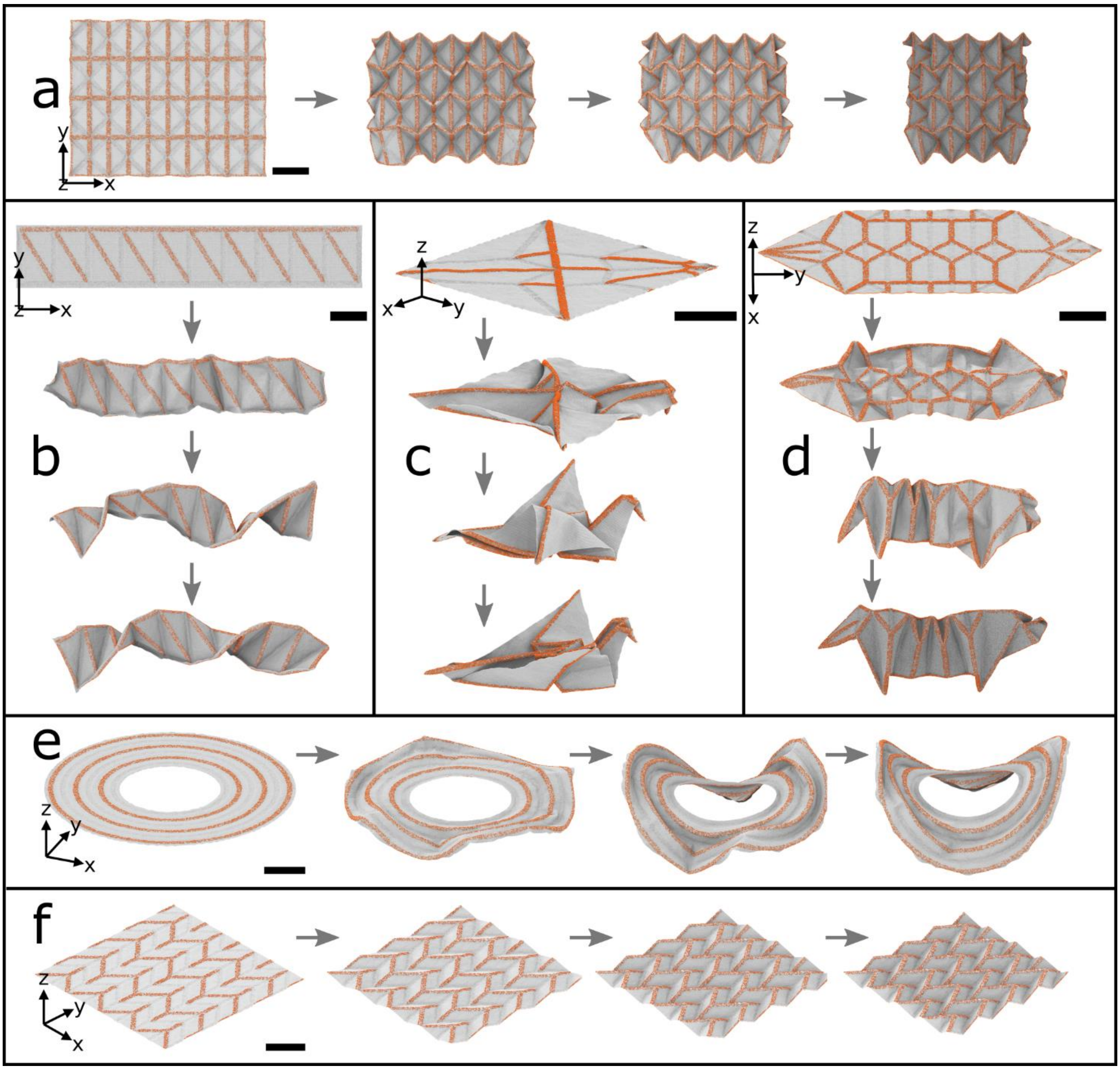

Figure S4: Emergence of complex 3D structures from graphene sheets by hydrogenation (Figures 1c and 3 in the main text). a: Water-bomb. b: Helix. c: Flapping bird. d: Dachshund dog, e: Saddle. f: Miura-ori . The scale bars are 20 nm.

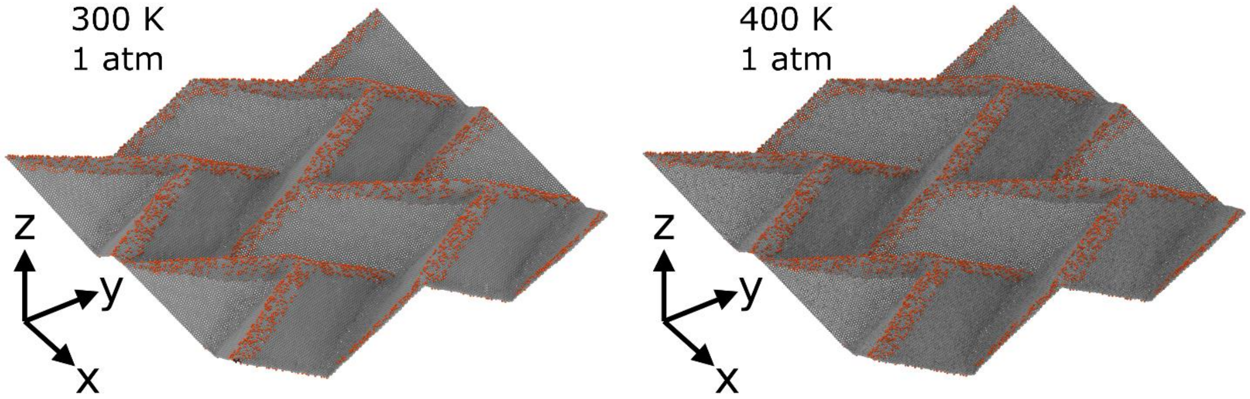

Figure S5: Equilibrated states (300 K, 400 K) of a graphene Miura-ori structure at 1 atm pressure for $w = 2.5$ nm and $\rho = 15\%$ (2×2 supercell of the dashed box in Figure 1a in the main text, 24.3 nm × 24.3 nm initial size of the simulation cell).

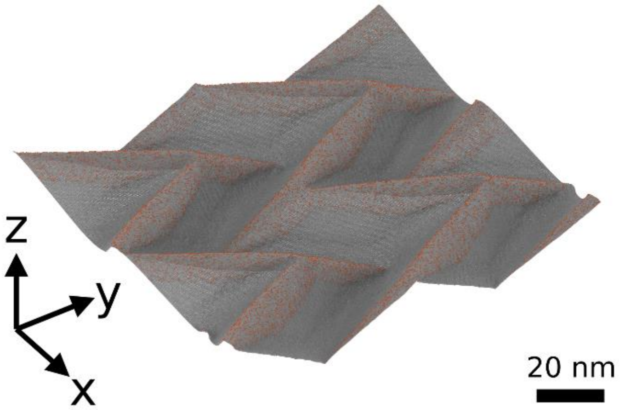

Figure S6: Equilibrated state (330 K) of a graphene Miura-ori structure for $w = 17.2$ nm and $\rho = 5\%$ (2×2 supercell of the dashed box in Figure 1a in the main text, 73.3 nm × 73.3 nm initial size of the simulation cell).

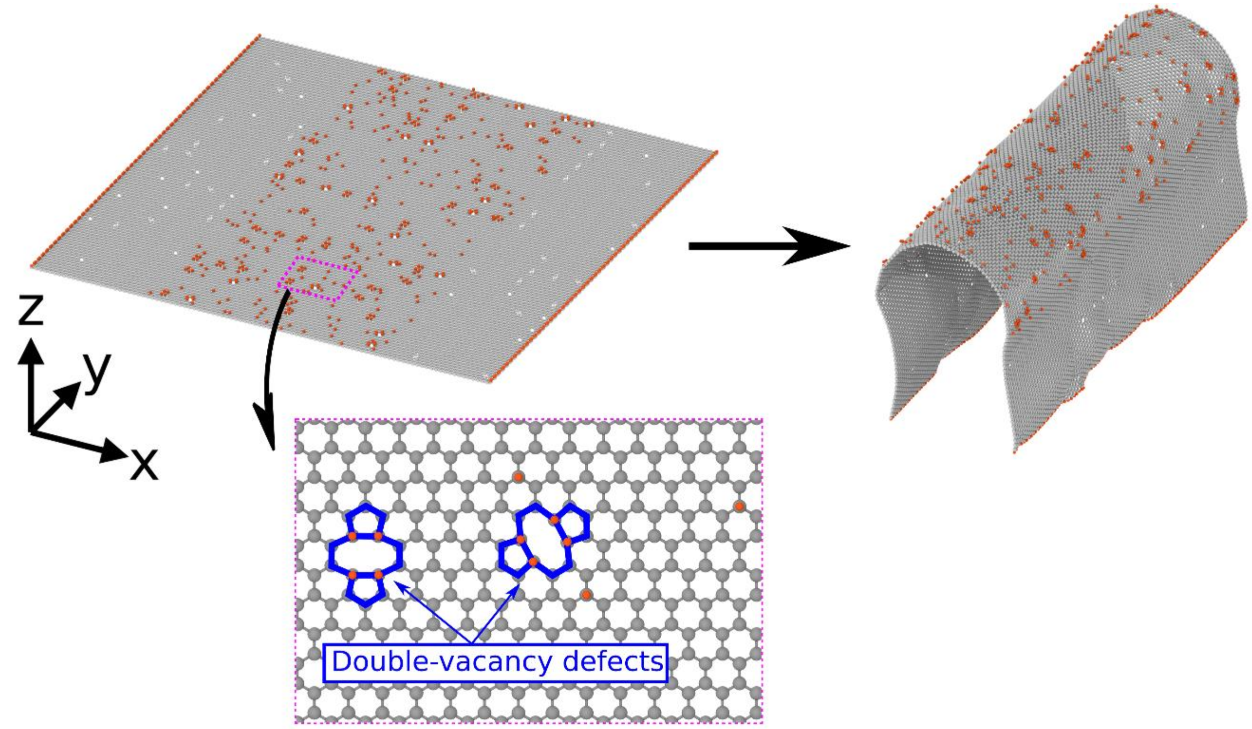

Figure S7: Folding of defective graphene at 1 K. Double vacancies are randomly generated with a density of 1%. The energetically favorable sites at the defects (on top of four carbon atoms) [3], are initially saturated with hydrogen atoms. The rest of the hydrogen atoms is distributed randomly. A periodic boundary condition is applied in the *y*-direction. $w = 12.3$ nm and $\rho = 5\%$.

References

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