Supporting Information

Effect of Copper Substrate Surface Orientation on the Reductive

Functionalization of Graphene

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Substrate	ω _G /cm ⁻¹	ω_{2D}/cm^{-1}	FWHM _G /cm ⁻¹	FWHM _{2D} /cm ⁻¹
Cu(111)	1596.5	2736.8	21.2	49.1
Cu(100)	1587.4	2718.4	21.8	39.3
p-Cu	1584.9	2712.4	20.7	29.7
SiO ₂	1582.9	2693.0	15.5	25.0

Table S1. Raman parameters of 1L graphene on different substrates (indicated).



Figure S1. SEM images of 1L graphene islands on (a, b) Cu(111), (c, d) Cu(100), and (e, f) *p*-Cu.

The morphology of the graphene islands was examined by scanning electron microscopy (SEM). The SEM image in Figure S1a shows uniform single layer graphene (1L) islands with regular hexagonal shapes on Cu(111). All hexagons are in the same orientation as a result of epitaxial growth on the Cu(111) substrate; these hexagonal islands are most likely single crystal graphene. The magnified SEM image in Figure S1b shows that the underlying Cu(111) substrate has regular step-like features. We note that the graphene region always shows the presence of these steps compared to the

relatively smooth bare Cu regions. We attribute this morphology to step bunching where smaller steps join to form a large step" during graphene growth.¹ No cracks or wrinkles can be observed in this island and on most other islands. Figure S1c shows hexagonal graphene islands grown on Cu(100), which are less uniform in orientation and in the number of layers. Wrinkles can be observed in such graphene, as shown in Figure S1d. Figure S1e shows islands on polycrystalline Cu (*p*-Cu), which have irregular shapes due to non-epitaxial growth. The white lines suggest the formation of cracks during post-CVD cooling. The underlying Cu substrate has an irregular step feature (Figure S1f). The cracks formed on graphene expose 'new' edges with a higher reactivity than the interior region.



Figure S2. Identification of the surface orientations of Cu substrates underlying the graphene after CVD growth, by EBSD. (a) Cu(111), (b) Cu(100) and (c) *p*-Cu.

The Cu surface lattice orientations after graphene growth were examined by electron backscatter diffraction (EBSD). Figure S2a shows a representative EBSD image of a 1L graphene island on Cu with a perfect (111) orientation (typical of all positions). The representative EBSD image of a 1L island on Cu in Figure S2b (typical of all positions) suggests a Cu surface orientation very close to Cu(100). For simplification, we use the term Cu(100) to designate this type of Cu substrate in this study. Figure S2c shows an EBSD image of a 1L island on p-Cu acquired at the boundary between two Cu grains with different orientations. Many other Cu orientations can also be observed for this type of Cu substrate. In addition, graphene islands on most p-Cu grains have similar shapes and Raman spectra. Therefore, the selected 1L island on p-Cu is representative of the majority of islands on p-Cu.



Figure S3. (a) Raman spectrum of a functionalized 1L graphene island on Cu(111) after heating at 450 °C for 2 h. (b) Line scan I_D/I_G ratios recorded from the heated sample. The inset optical image shows the scanned lines of two islands. (c) SEM image and (d, e) AFM image of functionalized 1L graphene islands on Cu(111) after heating at 450 °C for 2 h.

A functionalized 1L island on Cu(111) was heated at 450 °C under an argon atmosphere $(3 \times 10^{-1} \text{ Torr})$ for 2 h. The strong D peak observed in the functionalized graphene (Figure 1c) is no longer observed in Figure S3a. Instead, a broad peak appears in the range 1100–1400 cm⁻¹, which is attributed to the D peak of amorphous carbon formed

by the carbonization of hydrocarbons on graphene.² The asymmetric shape of the G peak also indicates the contribution from amorphous carbon to the Raman signals. The I_D/I_G ratio in Figure S3a, b is in the range of 0.07-0.23 and the I_D/I_G ratio of heated graphene is below 0.23. This result indicates that the thermal treatment of functionalized graphene regenerates the sp^2 -hybridized carbon lattice almost completely. Since other types of defects such as edges, basal plane vacancies or dopant atoms cannot be completely removed at 450 °C, the D peak observed in graphene after the reductive functionalization in this study should originate from sp^3 -hybridized carbon atoms.³ The surface morphology of the heated graphene investigated by SEM (Figure S3c) and AFM (Figure S3d, e) shows the existence of wrinkles, damage and impurities.



Figure S4. (a, b) Raman frequency (ω) maps of the (a) G and (b) 2D bands of the untreated 1L island on Cu(111) in Figure 2a. (c, d) (c) ω_G and (d) ω_{2D} maps of the untreated 1L island on Cu(100) in Figure 2b. (e, f) (e) ω_G and (f) ω_{2D} maps of the untreated 1L island on *p*-Cu in Figure 2c.

The Raman frequency (ω) maps in Figure S4 show that the 1L graphene island on Cu(111) has uniformly blue-shifted G and 2D bands over the whole area compared to that on Cu(100) and *p*-Cu. This observation suggests to us that 1L graphene on Cu(111) has a significant compressive strain.



Figure S5. Frequency maps obtained from the 1L island on Cu(111) in Figure 2a after the 3^{rd} functionalization run. (a) ω_{G} map. (b) ω_{2D} map.

Figure S5 shows that ω_G and ω_{2D} of 1L island on Cu(111) underwent redshifts after reductive functionalization, suggesting to us that the compressive strain in the graphene was partially relaxed.



Figure S6. (a) Raman spectra of continuous 1L graphene films on Cu(111) and *p*-Cu before functionalization. (b) Raman spectra recorded from graphene after attempted functionalization with iodobenzene. Reaction conditions: concentration of $[[K(15-crown-5)_2]Na]_0$ ($[C_{NaK}]_0$) = 0.02 M; $t_1 = 5$ min; $t_2 = 5$ min; temperature (T) = 20 °C. (c) Raman spectra recorded from graphene after functionalization with bromobenzene. Reaction conditions: $[C_{NaK}]_0 = 0.04$ M; t_1 = 10 min; $t_2 = 5$ min; T = 20 °C. (d-e) I_D/I_G maps of continuous 1L graphene films on (d) Cu(111) and (e) *p*-Cu after attempted functionalization with iodobenzene. Reaction conditions: $[C_{NaK}]_0$ = 0.02 M; $t_1 = 5$ min; $t_2 = 5$ min; T = 20 °C.

The differences in reactivity induced by the Cu substrate shown in Figures 1 and 2 for graphene islands were also observed for continuous graphene films. Figures S6a-c shows that continuous 1L graphene films on Cu(111) were functionalized to a higher degree than those on *p*-Cu when either iodobenzene or bromobenzene was used as the

reagent. The relatively uniform I_D/I_G map in Figure S6d suggests that the functionalization of a continuous 1L graphene on Cu(111) was uniform. In contrast, the I_D/I_G map in Figure S6e shows both functionalized and non-functionalized regions, indicating that the Cu substrate, rather than the size of the graphene, affects the functionalization.



Figure S7. Functionalization of graphene islands on Cu using lithium in a biphenyl reductive solution. (a) Scheme of the reductive functionalization. (b) I_D/I_G map of a functionalized 1L island on Cu(111). (c) I_D/I_G map of a functionalized 1L island on *p*-Cu. Reaction conditions: [C_{Li}]₀ = 0.2 M; t_1 = 2 min; t_2 = 5 min; T = 20 °C.

We attempted to functionalize 1L graphene islands on Cu(111) and *p*-Cu using a reductive solution prepared by dissolving lithium in a THF solution containing biphenyl. The I_D/I_G maps for each sample in Figure S7 show a reaction behavior similar to when using [K(15-crown-5)₂]Na (Figure 2).



Figure S8. (a, b) AFM height images acquired from (a) an unreacted island and (b) a reacted island on Cu(111). (c, d) AFM height images of (c) an unreacted island and (d) a reacted island on Cu(100). (e, f) AFM height images of (e) an unreacted island and (f) a reacted island on *p*-Cu. Reaction conditions: $[C_{NaK}]_0 = 0.02$ M; $t_1 = 5$ min; $t_2 = 5$ min; T = 20 °C; iodobenzene was used as a coupling reagent (see text).

The morphologies of 1L graphene islands on the three Cu substrates before and after functionalization (from the same batch of graphene shown in Figure 2 for each substrate) were examined by atomic force microscopy (AFM). Figure S8a shows the AFM image

of a typical unreacted island on Cu(111) with a measured surface roughness (R_a) of 4.1 nm in this area. Corrugated Cu steps are clearly seen in the region covered by the graphene; these steps are created by the bunching of smaller surface steps due to the presence of graphene. Our recent work explained that step bunching is enabled by the fast diffusion of metal adatoms underneath the graphene layer and is driven by the release of local bending energy of the graphene overlayer in the vicinity of surface steps on the metal surface.¹ Such islands have few to no wrinkles in contrast to islands grown on a *p*-Cu surface under the conditions of our AFM measurement. The presence of Cu steps and the absence of wrinkles as well as further details on the compressive strain in such samples were discussed in a previous paper.⁴ The reductive functionalization led to a more distinct contrast between the graphene-covered region and the bare Cu in Figure S8b, which is most likely due to the presence of phenyl groups as well as, perhaps, some physically adsorbed molecules. The functionalization of this island on Cu(111) is relatively uniform and typical for many islands. Since many graphene wrinkles are observed in the functionalized sample, we surmise that the wrinkles are created due to the relaxation of compressive strain from functionalization. Figure S8c shows an AFM image of a typical unreacted island on Cu(100) with a measured R_a in this area of 3.8 nm. The fact that the bare Cu(100) surface lost its crystal terraces may be due to minor oxidation when exposed to air, which makes the edges of the graphene islands clear. Wrinkles can often be observed in such samples, as also seen in the SEM image in Figure S1d. After functionalization, while most regions of the graphene island remained unchanged, some areas became rougher, possibly due to non-uniform functionalization. Such non-uniformity in functionalization was also observed for a graphene island on *p*-Cu. Figure S8e shows a representative image of an island on *p*-Cu ($R_a = 8.0$ nm). Some lines that are similar to graphene edges are found in the interior region, and these are likely either graphene boundaries formed during the growth or newly-formed edges due to 'cracking' (fracture) of the film. Although the Raman I_D/I_G map cannot detect such lines in unreacted graphene, a high reactivity at these locations is still expected. After functionalization, the Raman maps of the edge and boundary regions of the island differ from that of the interior region (Figure S8f), indicating a non-uniform reaction. Since the roughness of these graphene islands is of the same scale, the influence of surface roughness (on this scale) in reductive functionalization is evidently less important, or even negligible, compared to other factors.

Computational details

Molecular dynamics (MD) simulations

All-atom molecular dynamics (MD) simulations were performed with the COMPASS II force field in the Forcite program⁵ to describe the interaction between a graphene flake and the Cu substrate (111) surface. The atom-based summation method was used for the short-range van der Waals interactions with a cut-off distance of 15 Å. Long-range electrostatic interactions were computed using the Ewald summation method with an accuracy of 1×10^{-4} kcal/mol.^{6,7} The *NVT* (i.e., canonical ensemble) MD simulation was performed with the Berendsen thermostat at room temperature for 1 ns with a time step of 1 fs.⁸

As shown in Figure S9, regular hexagonal graphene with a hydrogenated zigzag edge composed of 1,944 carbons, 108 hydrogens, and a 9-layer periodic Cu(111) substrate of 15,444 copper atoms (9.73 nm \times 9.96 nm) were used. The height of the simulation box was extended to 50 nm along the *z*-direction to avoid self-interaction. Note that the two lowest Cu layers were fixed to represent the bulk phase. A Hirshfeld charge,⁹ obtained from DFT calculation (Figure S10), was applied to the geometrically optimized system.

Density functional theory (DFT) calculations

Density functional theory (DFT) calculations using the DMol³ program were used to elucidate the effect of compressive strain on graphene covalent functionalization.^{10,11}

The generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) functional¹² was used while a long range dispersion correction accounting for the van der Waals interaction was implemented by Grimme's D2 method.¹³ The spin-polarized calculation was used with double numerical plus polarization (DNP) of the 4.4 level as the basis set. Core treatment was conducted with density functional semicore pseudopotentials¹⁴ with a global orbital cutoff radius of 5.6 Å and a smearing value of 0.005 Ha. The Brillouin-zone was sampled by a $1 \times 1 \times 1$ *k*-point using the Monkhorst-Pack scheme.¹⁵ A transition state (TS) search calculation was used with the conjugated the kinetic barrier to the covalent functionalization of graphene, where the linear and quadratic synchronous transit (LST/QST) method was used with the conjugated gradient (CG) refinement¹⁶ with 0.01 Ha/Å for RMS convergence. An implicit THF environment was achieved by using a conductor-like screening model (COSMO) scheme¹⁷ with a dielectric constant of 7.47 (THF at 20 °C¹⁸).

For the reactants of the covalent functionalization of graphene, single layer graphene consisting of 98 carbon atoms, was located in the simulation box (i.e., $17.3 \times 17.3 \times 40.0$ Å³ for unstrained 7×7 graphene supercells), where a vacuum region perpendicular to the graphene (along the *z*-direction) was introduced (i.e., 30 Å) to minimize self-interaction (Figure S11a). 15-crown-5, Na, K, and iodobenzene were introduced as the reactants to facilitate the covalent functionalization of graphene (Figure S11b). To investigate the effect of compressive strain on the reaction, we applied -0.1, -0.2, -0.3, -0.4, and -0.5 % biaxial strains to the graphene. The phenyl group in iodobenzene was chemically adsorbed on the graphene after breaking the bond between the halogen atom

and the phenyl group. The 15-crown-5, Na, K, and I species as well as the functionalized graphene were fully optimized after the adsorption of the phenyl group on the graphene.



Figure S9. Structure of the graphene flake on Cu(111) used in the MD simulation. The white and orange spheres represent the H and Cu atoms, respectively. The dark-gray honeycomb network represents a layer of graphene.



Figure S10. The optimized structure of a periodic graphene/Cu system consisting of single layer graphene and 4-layer Cu substrate. The numbers in the right panel are the averaged Hirshfeld charge for each layer. Orange spheres are Cu atoms. The dark-gray honeycomb network is a part of the graphene layer. The bottom Cu layer was fixed to represent the bulk phase.



Figure S11. The structures of (a) graphene, (b) 15-crown-5, K, Na, and iodobenzene used in the DFT calculations. White, red, light blue, purple, blue, and gray spheres represent H, O, K, Na, I, and C atoms respectively. The dark gray honeycomb network represents a layer of graphene.



Figure S12. Top view of the lowest energy structures of (a) a graphene flake, which was functionalized with a phenyl group, on top of a Cu (111) substrate and (b) a graphene flake functionalized with a phenyl group under different degrees of compressive strain (indicated). The outermost carbon atoms of the graphene flakes were constrained during the geometry optimization process to describe a pristine or compressed graphene lattice. Orange, gray, and white balls represent Cu, C, and H atoms, respectively. The COSMO method was used to account for solvent effects and to calculate the dielectric constant of THF.

The binding energies between the functionalization reagent and a graphene flake under increasing compressive strain and in the presence of the Cu substrate were also calculated (Figure S12). The data indicated that the Cu substrate increased the binding strength by approximately $0.34 \sim 0.37$ eV (Table S2).

Table S2. Binding energy $(E_{binding})$ of a phenyl group on a graphene flake with or without a Cu substrate at 0.00, -0.30, and -0.50 % strain. Note that the binding energy was estimated by the energy released after the adsorption of the phenyl group on the graphene $(E_{binding} = E_{total} - (E_G \text{ or } E_{G/Cu} + E_{phenyl group})$. The total energy of the phenyl -adsorbed system on the graphene flake is expressed as E_{total} while the total energies of the graphene flake, the graphene flake with a Cu substrate, and the phenyl group are expressed as E_G , $E_{G/Cu}$ and $E_{phenyl group}$, respectively.

Strain	Graphene flake/Cu	Graphene flake
0.00 %	-1.4825 eV	-1.1414 eV
-0.30 %	-1.5055 eV	-1.1483 eV
-0.50 %	-1.5195 eV	-1.1546 eV

To investigate the energetic relation between graphene deformation and the interactions formed between graphene and Cu(111), DFT calculations were performed using graphene flake models (Figure S12). The results are shown in Table S3. It was found that the deformation energy of graphene decreased as applied compressive strain increased. Also, the binding energy between graphene and the Cu substrate decreased as the compressive strain increased. Thus, the deformation energy of the graphene becomes lower with increasing compressive strain while interaction between graphene and Cu substrate is weakened. Table S3. Deformation energy (E_{deform}) of graphene on a Cu substrate and the binding energy ($E_{G/Cu_binding}$) between graphene and the Cu substrate at 0.00, -0.30, and -0.50 % strain. Note that the deformation energy was estimated by the energy required by the graphene for the structural change of the functionalization reaction ($E_{deform} = E_{G_deform} - E_{G_relaxed}$). The total energy of the graphene flake in the deformed state on Cu is expressed as E_{G_deform} and the total energy of the relaxed graphene flake on Cu is expressed as $E_{G_relaxed}$. The binding energy between graphene and Cu substrate was calculated by $E_{G/Cu_binding} = E_{G/Cu} - (E_G + E_{Cu})$, where the total energies of the graphene flake with a Cu substrate, an isolated graphene flake and the underlying Cu substrate are expressed by $E_{G/Cu}$, E_G and E_{Cu} , respectively.

Strain	E _{deform}	$E_{G/Cu_binding}$
0.00 %	1.3103 eV	-0.1589 eV/atom
-0.30 %	1.3078 eV	-0.1566 eV/atom
-0.50 %	1.3037 eV	-0.1551 eV/atom



Figure S13. Raman spectra of 1L islands on Cu(111) functionalized for different periods of time (t_2).

Figure S13 shows the spectra of 1L islands on Cu(111) reacted for different times in the second step (t_2). It is seen that t_2 does not influence the functionalization degree; this result is accordance with previous conclusions on the functionalization of graphene on SiO₂/Si.³



Figure S14. (a) The average reaction rate (represented by defect density (n_D)/t₁) as a function of *T*.
(b) Relationship between ln*k* and 1/*T*. Error bars represent the standard deviations.

It is known that the change in the graphene Raman spectrum with increasing defect density (n_D) shows two typical stages.¹⁹⁻²² In stage I, where n_D is relatively low, I_D/I_G

increases with increasing n_D due an increase in the defect-activated D peak. At this stage, the D and 2D peaks are relatively sharp and the defect density n_D can be calculated from equation $(1)^{21}$

$$n_{\rm D} (\rm cm^{-2}) = (7.3 \pm 2.2) \times 10^9 E_{\rm L}^4 (\frac{l_{\rm D}}{l_{\rm G}})$$
 (1)

where E_L is the laser energy (in electron volts). In stage II when n_D is relatively high due to the overlap of different defect-activated regions,²² the D peak becomes broad and less intense. As a result, I_D/I_G decreases with increasing n_D . In addition, the 2D peak is very weak and broad in stage II, in contrast to the narrow peak in stage I, which means that in stage II, n_D cannot be calculated from I_D/I_G . ¹⁹⁻²² By comparing the data in Figures 5c, d with the changes in the Raman spectra (n_D), the spectra of 1L islands functionalized at T = 10 °C; $t_1 = 10$ or 20 min (Figure 5c) and at T = 10 or 20 °C; $t_1 =$ 10 min (Figure 5d), can be assigned to stage II. The lower I_D/I_G values with increased t_1 (Figure 5c) or T (Figure 5d) are due to an increase in n_D .

The reductive functionalization of graphene is a process that occurs at the graphenesolution interface. To better understand the kinetics deduced from experimental data, several assumptions were made.

(1) Since [K(15-crown-5)₂]Na and iodobenzene are in excess, we assume that the concentrations of [K(15-crown-5)₂]Na and iodobenzene do not influence the degree of functionalization on Cu(111). A similar result was obtained for continuous graphene films on Cu(111).

- (2) In principle, with more phenyl groups being attached to graphene, the reaction rate (*r*) is lowered due to a decrease in the density of sp^2 -C atoms (n_C) in graphene as well as due to steric hindrance from the attached groups. As a result, the functionalization may saturate when t_1 is long enough. However, for low degrees of functionalization, designated by 'Raman stage I', one can assume that both the decrease in n_C and the steric hindrance are low. Indeed, the maximum functionalization degree in stage I given by equation (1) is only ~0.2%.
- (3) All defects are sp^3 -C type, which means that equation (1) can be used to quantify the number of sp^3 -C atoms in the functionalized graphene.

With the above assumptions, the reaction rate r can be calculated using equation (2):

$$r = \frac{\mathrm{d}n_{\mathrm{D}}}{\mathrm{d}t_{1}} = k(T)n_{\mathrm{C}}^{m} \tag{2}$$

where k is the reaction rate constant, $n_{\rm C}$ is the density of non-functionalized carbon atoms, which is a constant according to assumption (2), and m is the reaction order. If we simplify the average reaction rate $r_{\rm a}$ to be r, according to equation (1), the relationship between r and T can be plotted as shown in Figure S14a. Note that the two $I_{\rm D}/I_{\rm G}$ values of graphene functionalized at T = 10 or 20 °C ($t_1 = 10$ min) were not used in the calculation because the corresponding Raman spectra are in stage II.

The Arrhenius equation (3) can be considered for the reductive functionalization:

$$k(T) = Ae^{-\frac{E_a}{RT}}$$
(3)

where *A* is the pre-exponential factor, E_a the activation energy, and *R* the universal gas constant.

By combining equations (2) and (3), one obtains equation (4):

$$\ln k = \ln A - \frac{E_a}{RT} = \ln \left(\frac{n_D}{t_1}\right) - m \ln n_C \tag{4}$$

Replacing $n_{\rm C}^{-m}$ by A_0 , which is a constant from the aforementioned assumptions, equation (4) can be stated as:

$$\ln\left(\frac{n_{\rm D}}{t_1}\right) = \ln k - \ln A_0 = -\frac{E_a}{RT} + \ln A \tag{5}$$

From the relationship between n_D/t_1 and T shown in Figure S14a, $\ln k - \ln A_0$ was obtained as a function of 1/T as shown in Figure S14b. The three curves obtained at $t_1 = 2$, 5 and 10 min were fitted to straight lines (Figure S14b). E_a values from the slopes of the fitted lines are 19.6 ± 2.0, 22.9 ± 3.2, and 21.7 ± 5.4 kJ·mol⁻¹ for $t_1 = 2$, 5 and 10 min, respectively. Therefore, the activation energy for the reductive phenylation of 1L islands is estimated to be around 20 kJ·mol⁻¹.



Figure S15 The graphene island on Cu(111) shown in Figure 6a before functionalization. (a) Optical image, (b) AFM height image and (c) Raman I_{2D}/I_G , (d) FWHM_{2D}, (e) ω_D and (f) ω_{2D} maps.

Optical and AFM images of the graphene island on Cu(111) shown in Figure 6 are shown in Figures S15a, b, where four regions including bare Cu(111) (bottom right), 1L, AB-stacked bilayer (AB2L) and mis-oriented bilayer (m2L) regions can be distinguished. Three types of graphene have been assigned based on Raman spectroscopy data as shown in Figure 6a and Figures S15c, d.^{23,24} For example, from their characteristic correlations between G and 2D band intensities, 1L, AB2L and m2L regions respectively are shown in blue ($I_{2D}/I_G = 1.3$), purple ($I_{2D}/I_G = 0.6$) and green ($I_{2D}/I_G = 2.0$) in the I_{2D}/I_G (height) map (Figure S15c). The two layers in the m2L region

have a rotation angle of $\sim 30^{\circ}$ to each other (Figure S15b). Indeed, a rotation angle of $\sim 0^{\circ}$ or 30° was observed frequently for our BLG islands on Cu(111), while other angles were rarely observed. From the optical and AFM images in Figure S15a, b, it is noted that the AB2L region shows higher steps than the m2L region, which helps in the relaxation of compressive strain. The lower G and 2D frequencies of 2L than 1L shown in Figures S15e, f suggest that the compressive strain in 2L is weaker than in 1L graphene. In addition, when compared to AB2L, m2L has a slightly blue-shifted G band, as well as a red-shifted 2D band.



Figure S16. The evolution of strain of a graphene island on Cu(111) with reaction time t_1 .

In the case of 2L graphene, we used the G band to estimate the compressive strain. The calculated strain map of the graphene island in Figure S15 at each stage of functionalization is shown in Figure S16. Before reaction, the sequence of compression is 1L > m2L > AB2L in this graphene island. All three types of graphene underwent partial compression release during the reaction.



Figure S17. (a) Optical image (b), Raman G band intensity map and (c) Raman spectra recorded at the positions marked in (b) of the AB2L/3L island on Cu(111) before the reaction. (d) Optical image, (e) Raman I_{2D}/I_G map and (f) Raman spectra recorded at the positions marked in (e) of the m2L island on Cu(111) before the reaction.

We have also studied the functionalization of individual AB2L/3L (consisting of both 2L and 3L regions) and m2L graphene islands on Cu(111). Figure S17a shows a hexagonal graphene island with a smaller hexagon inside. Higher step-bunching in the smaller hexagon and the parallel edges of the two hexagons suggest that the smaller region is few-layer graphene. The Raman G map (Figure S17b) and spectra (Figure S17c) clearly shows that this island contains 1L, 2L and 3L graphene with AB-stacking in the few-layer region. In contrast, Figure S17d shows an island containing 1L and m2L graphene regions. Figure S17e clearly shows the misoriented stacking as indicated

by the characteristic I_{2D}/I_{G} ratio as well as the rotation angle (30°) between the two layers.



Figure S18. (a, b) AFM height images of the AB2L/3L graphene island on Cu(111) shown in Figures S17a-c. (c, d) AFM height images of the m2L island on Cu(111) shown in Figures S17d-f.

AFM images of the same AB2L/3L island and m2L island on Cu(111) in Figure S17 are shown in Figure S18. In addition to similar AFM information given in Figure S15b, more wrinkles can be observed for the AB2L/3L island in the magnified AFM image.

The formation of these wrinkles helps release the compressive strain in AB-stacked few-layer graphene.



Figure S19. (a, b) Raman (a) ω_{G} and (b) ω_{2D} maps of the AB2L/3L island on Cu(111) before functionalization. (c, d) Raman (c) ω_{G} and (d) ω_{2D} maps of the m2L island on Cu(111) before functionalization.

Raman ω_{G} and ω_{2D} maps (Figure S19) of the AB2L/3L and m2L islands show similar features as discussed in Figure S15. From the G band, one can estimate compressive strains of -0.08% and -0.11% for AB2L/3L and m2L, respectively. The higher compression of m2L is in line with its fewer wrinkles than AB2L/3L, as shown in Figure S18.



Figure S20. (a, b) I_D/I_G maps of (a) the AB2L/3L island on Cu(111) and (b) the m2L island on Cu(111) before and after functionalization with different t_1 times for three runs.

Figure S20 shows the evolution of the reductive functionalization of the AB2L/3L and m2L islands (see Figures S17-S19) with the reaction time t_1 . Similar to the discussion on Figure 6, m2L shows a higher degree of functionalization than AB2L/3L graphene. In addition, 3L has a lower reactivity than 2L graphene.



Figure S21. Raman I_D/I_G distributions of functionalized 1L islands on Cu(111) using 15-crown-5, 18-crown-6 or cryptand-222. Reaction conditions: iodobenzene: $[C_{NaK}]_0 = 0.02$ M; $t_1 = 5$ min; $t_2 = 5$ min; T = 20 °C; bromobenzene: $[C_{NaK}]_0 = 0.02$ M; $t_1 = 10$ min; $t_2 = 5$ min; T = 20 °C.

We have also investigated the effect of macrocyclic ligands on the reductive functionalization of graphene on Cu(111). In principle, a macrocyclic compound capable of coordinating with an alkali cation should facilitate the dissolution of the alkali metal/alloy to form an alkalide solution. The coordination efficiency likely determines the dissolution rate and stability of the alkalide solution, which consequently alters the functionalization efficiency. In addition to 15-crown-5, we prepared solutions that contained 18-crown-6 or cryptand-222 along with NaK in THF, and then used these solutions to reduce the 1L graphene islands on Cu(111) (see the experimental section). We found that while cryptand-222 resulted in a degree of functionalization that was close to that of 15-crown-5, 18-crown-6 led to a lower reactivity irrespective of whether iodobenzene or bromobenzene was used as the

reagent (Figure S21). It has been reported that the sandwich-like $[K(15\text{-}crown-5)_2]^+$ complex has a higher stability than the planar $[K(18\text{-}crown-6)]^+$ complex, which is attributed to the participation of more oxygen atoms in the coordination with potassium cations.²⁵ On the other hand, cryptand-222 has a three-dimensional interior cavity, which may render it more selective than 18-crown-6.²⁶ Regardless, 18-crown-6 exhibited the lowest reaction efficiency of the three ligands explored. Based on these results, we conclude that the degree of functionalization may be influenced by the macrocyclic additive.

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