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Supporting Materials: Atomic Layer Deposition Growth and Characterization of Al_2O_3 Layers on Cu-Supported CVD Graphene

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I. Graphene growth parameters.

1. Single-layer graphene.

Annealing stage				Growth stage			
Temperature	**Gases**	**Ratio**	**Time**	**Temperature**	**Gases**	**Ratio**	**Time**
1050 °C	**H_2/Ar**	**1:10**	**30 min.**	**1050 °C**	**CH_4/H_2/Ar**	**1:5:150**	**30 min.**

2. Bilayer graphene.

Annealing stage				Growth stage			
Temperature	**Gases**	**Ratio**	**Time**	**Temperature**	**Gases**	**Ratio**	**Time**
1050 °C	**H_2/Ar**	**1:10**	**30 min.**	**1050 °C**	**CH_4/H_2/Ar**	**0.1:5:150**	**10 min.**
						1:8:150	**25 min.**

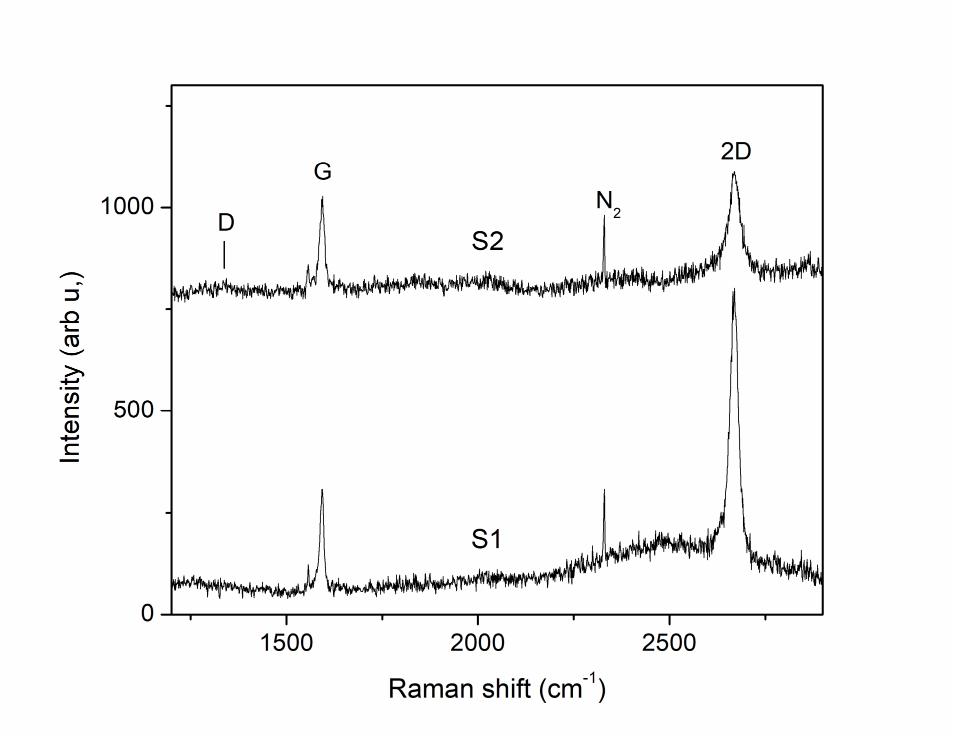

Figure S1. Representative Raman spectra for the graphene grown on samples S1 and S2.

From the collected Raman spectra of as-grown Cu-supported graphene, we obtained values for the peak intensity ratio of the 2D and G band I(2D)/I(G) of about 1 – 1.2 for sample S1 and about 2.5 – 2.8 for sample S2. These values can, however, be impacted by the graphene–Cu coupling; therefore, they can only be regarded as a qualitative indicator. On the other hand, it is widely accepted that monolayer graphene yields an I(2D)/I(G) value of about 3 and bilayer graphene yields a I(2D)/I(G) value of about 1 or between 1 and 2. In view of the sharp difference of the two obtained ranges, we can thus safely assume the presence of predominantly single-layer graphene for S1 and predominantly bilayer graphene for S2.

II. Additional AFM and SEM results for sample S2 with 116 nm Al_2O_3:

From the SEM images of sample S2 with the thicker Al_2O_3 layer, two types of surface morphology stand out (see Figure S2): relatively smooth plateaus (see lower left corner of Fig. S2 (a)) surrounded by terraced step-like structures, exhibited in both Fig. S2 (a) and (b). Examination of these two morphology types by AFM, shown in Fig. S2 (c) and (d), reveals an RMS roughness of about 2 and 8 nm, respectively.

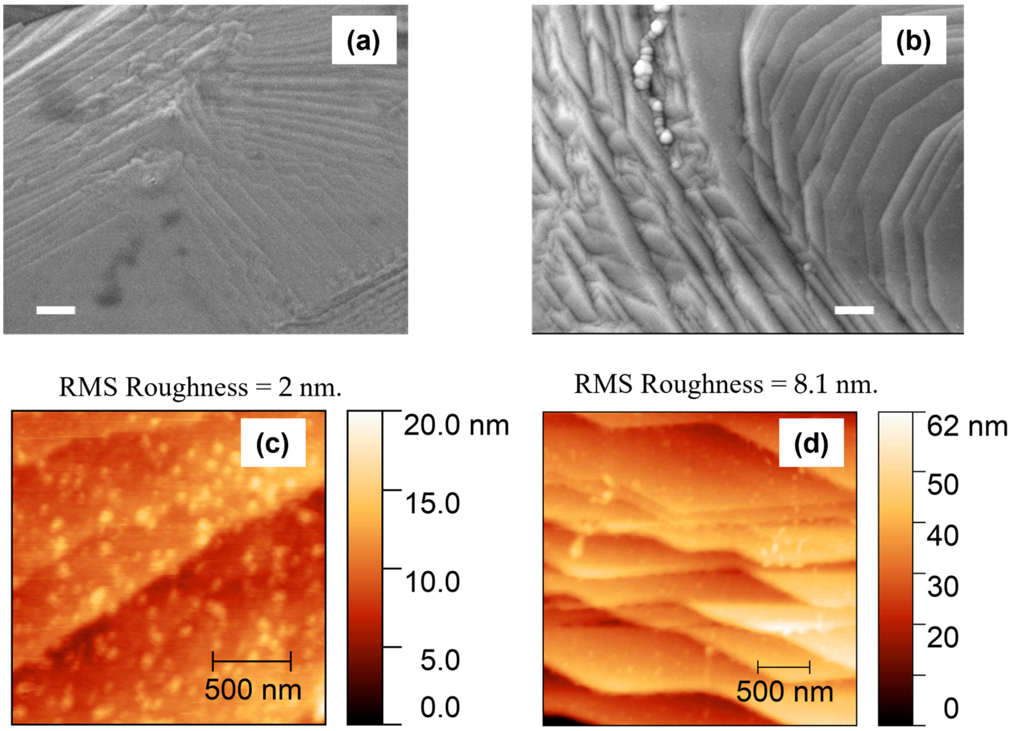

Figure S2. Additional SEM ((a) and (b)) and AFM ((c) and (d)) images of sample S2. The scale bar in images ((a) and (b)) represents 500 nm.

III. Study of the impact of aging and testing the effect of the Al_2O_3/graphene heterostructure as an anti-corrosion protectant.

Prompted by the observation that the Cu-substrate surface survives the Al_2O_3 ALD growth without Cu_2O formation, we stored a part of sample S1 with the predominantly monolayer graphene and 40 nm thick Al_2O_3 layer for three years to study the impact of aging. This part contains a specific defect on the Cu surface, which enables its repeated location under an optical microscope. Fig. S3 depicts the appearance of the lower part of the region shown in Fig. 7(b) and (c) of the main article after three years. Initial patches of Cu_2O formation are recognizable by their red color [39], presumably due to penetration of air humidity through cracks in the aged Al_2O_3 coating and Cu grain boundaries. Nevertheless, such an initial oxidation stage of the Cu surface is remarkable because an analogous chemical transformation takes place on a Cu foil with only CVD graphene grown on it in the matter of a few weeks [39]. Figure S4 shows the corresponding Raman spectra (red traces) measured at the same spots marked with consecutive numbers and the symbol "GC" as in Fig. 7 (b) in the main article. As seen from Fig. S3, most of these spots are not yet oxidized, which is confirmed by the low intensity and the only insignificantly compensated blue shift of the G and 2D bands in the red spectra, as well as by the lack of Cu_2O bands in them. There is, however, an increase in the G and the 2D band widths and the D-to-G intensity ratio which we attribute to a slow post-ALD process of covalent bond formation between the graphene and the adsorbed molecules from the ALD pretreatment stage. This explanation is supported by the fact that the slight softening of the G and 2D band is accompanied by a decrease in their intensity, implying weakening of the resonant scattering mechanism which is not related to the Cu-graphene coupling but rather to the increasing structural disorder in the graphene lattice.

Figure S5 shows the spectra displayed in red in Fig. S4 together with two spectra from oxidized spots (recognizable by the reddish coloring in Fig. S3) for comparison. The G and the 2D frequencies in these spectra exhibit significant softening towards their strain-free values induced by the relaxation of the Cu-graphene coupling [39]. As the oxidized area is small in comparison to the whole area depicted in Fig. S3, we can conclude that, in contrast to other oxide deposition processes that directly oxidize the substrate [44], the applied Al_2O_3 ALD growth on Cu-supported graphene creates a heterostructure that can serve as long-term anti-corrosion protection for the Cu substrate.

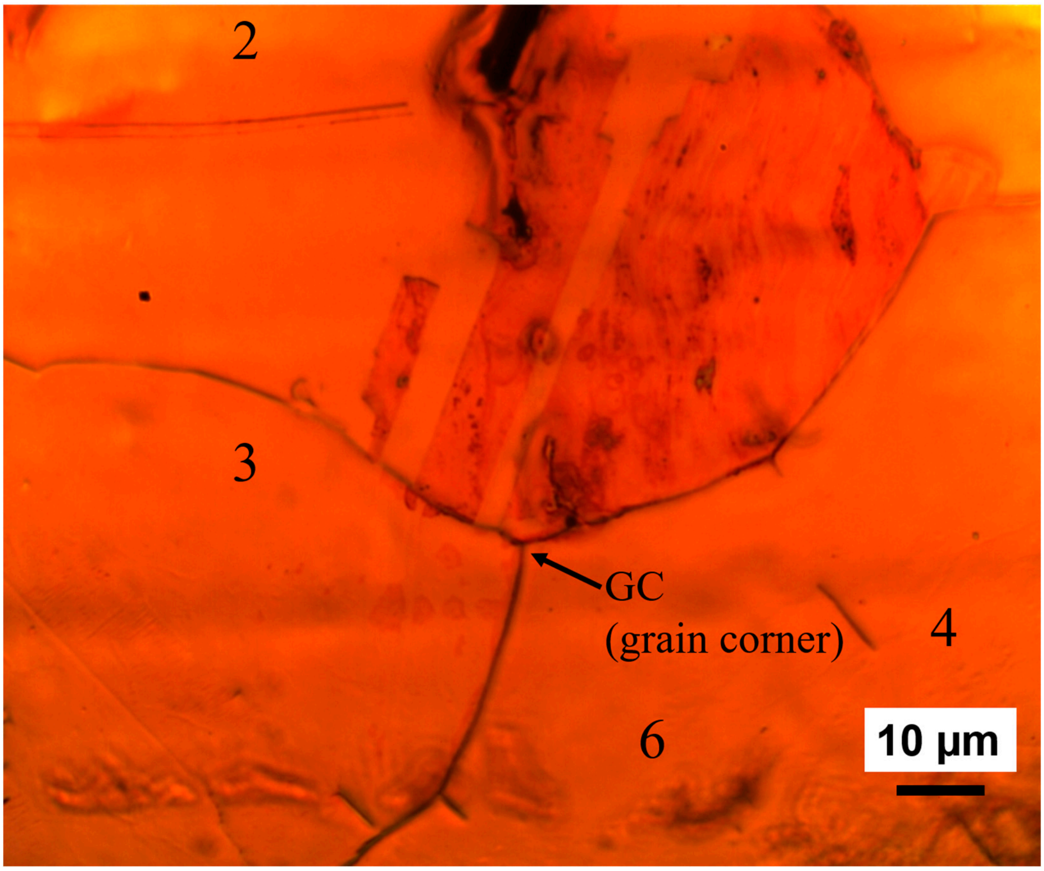

Figure S3. Optical micrograph of the lower part of the region depicted in Fig. 7(b) and (c) of the main article, taken after a period of three years. Spots of the Raman measurements are marked with consecutive numbers and the symbol "GC" according to the corresponding labels in Fig. 7(b).

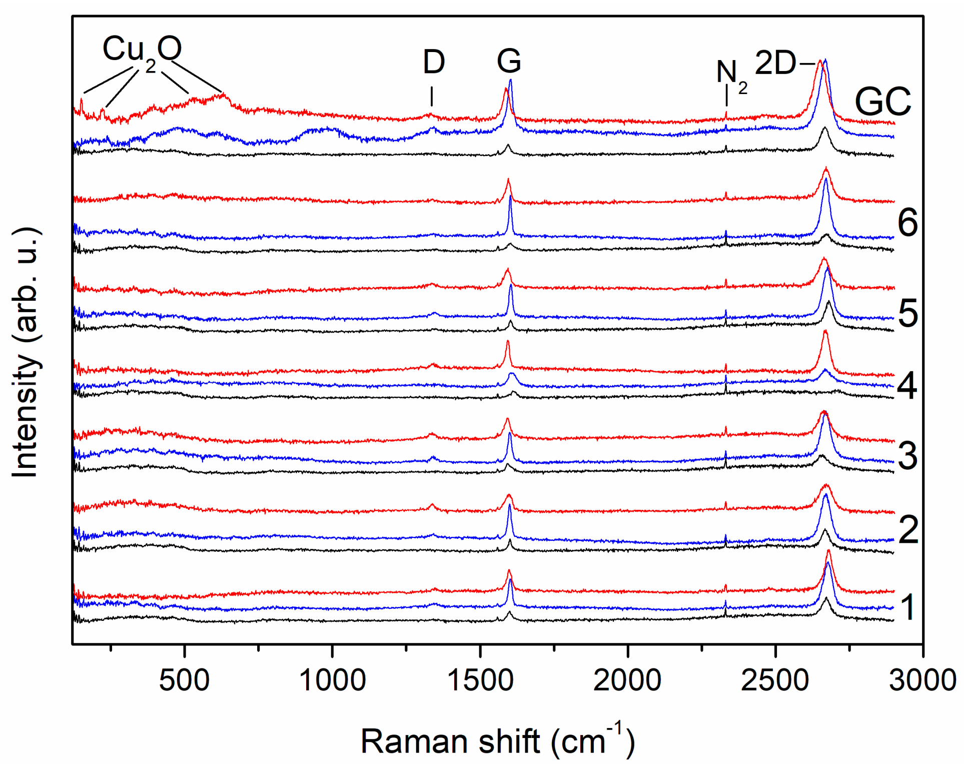

Figure S4. Same Raman spectra from Figure 7(a) in the main article shown to the full extent (100 – 2900 cm^{-1}), with added Raman spectra (red traces) measured at the same spots after 3 years.

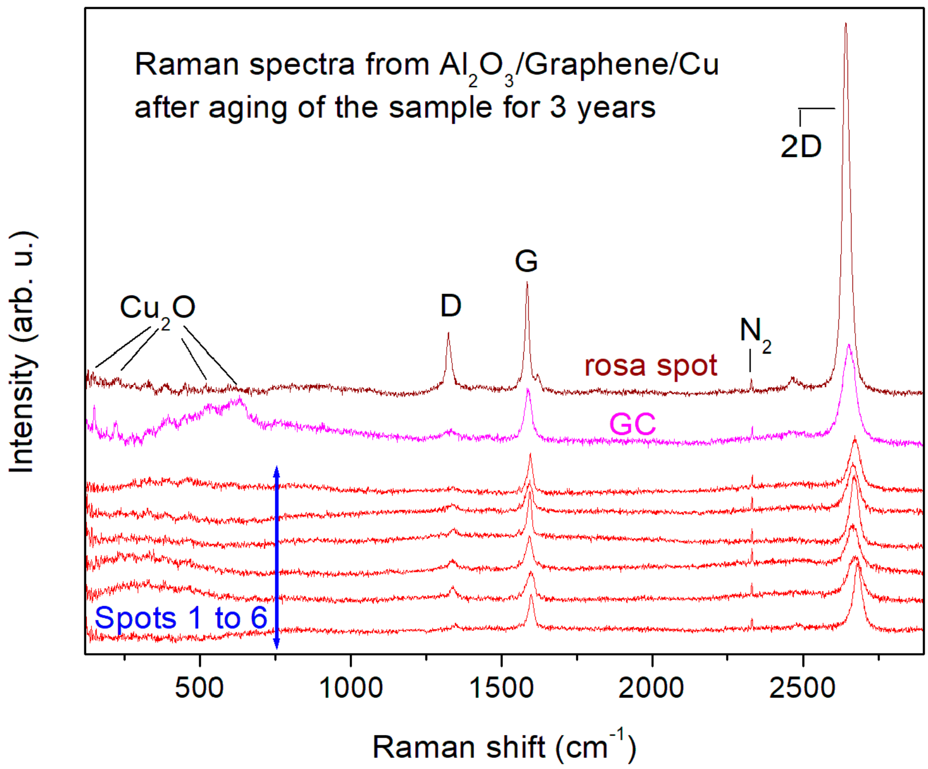

Figure S5. Raman spectra depicted in red with labels 1 - 6 in Figure S4 (red) shown together with two spectra measured at oxidized spots and labelled "GC" (magenta) and "rosa spot" (brown).