Supporting Information

Atomic Structures of Pt Nanoclusters Supported on Graphene Grown on Pt(111)

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Figure S1 shows the LEED pattern from a graphene/Pt(111) surface. The graphene was grown on exposing Pt(111) to ethylene (300 L) at 950 K. The six sharp spots

come from Pt(111) substrate, corresponding to the six-fold symmetrical structure. The outer arc- shape spots and the faint spots in line with the Pt spots are from the graphene layer. The centers of the arc-shape spots are rotated by an angle of 30° relative to the spots from Pt(111). The result resembles earlier ones from the graphene/Pt(111) prepared under a similar condition.[1,2] This observation does not agree entirely with that by using RHHED. The RHHED patterns show the diffraction intensities from $\mathbf{G_{0°}}$ and $\mathbf{G_{30°}}$ are comparable, whereas the LEED patterns show that the intensity from $\mathbf{G_{30°}}$ is stronger than that from $\mathbf{G_{0°}}$.

Figure S2(a) shows the DFT modelling for $\mathbf{G_{0°}}$, the corrugated graphene sheet. The upper part of Figure S2 shows the side view through direction $[1\bar{1}00]$ of the graphene and direction $[\bar{1}10]$ of the Pt(111) surface, and the lower part the top view. The side view clearly indicates the carbon (C) atoms are not all at the same level: some are higher and some lower. The graphene sheet corrugated a little, due to its strong interaction with the Pt(111) surface. The strong interaction is also reflected in the graphene *p* band in the antibonding regime. Figure S2(b) compare the DOS of the *p* bands of C atoms from the grown graphene on Pt(111) and free-standing graphene. The *p* band of $\mathbf{G_{30°}}$ (flat and with no corrugation) resembles that of free-standing graphene, implying a weaker interaction between $\mathbf{G_{30°}}$ and Pt(111), whereas that of $\mathbf{G_{0°}}$ differs evidently in the antibonding regime (Energy ≥ 0). As the *p* band in the

antibonding regime involves the interaction with Pt(111), the evident difference indicates a strong $\mathbf{G_{0°}}$-Pt(111) interaction.

Figure S3 shows the DOS analysis of the *d* bands of the Pt adlayers in $\mathbf{Pt_{0°}/G_{0°}}$ and $\mathbf{Pt_{0°}/G_{30°}}$. The *d* band center of the Pt adlayer in $\mathbf{Pt_{0°}/G_{0°}}$ has a lower energy (-2.91 eV) whereas that in $\mathbf{Pt_{0°}/G_{30°}}$ has a higher one (-2.33 eV); the latter is closer to that for an isolated Pt layer (black line in Figure S3). Additionally, the DOS line of the *d* band for the Pt adlayer in $\mathbf{Pt_{0°}/G_{30°}}$ also resembles more that for an isolated Pt layer. Both these features suggest that the Pt adlayer-graphene interaction in $\mathbf{Pt_{0°}/G_{0°}}$ is stronger.

Figure S4(a) shows optimized structures and induced charges of Pt adlayers on the graphene/Pt(111) surfaces. The Pt adlayers were initially arranged to have a rotation of 30° with respect to the beneath Pt lattice, $\mathbf{Pt_{30°}/G_{0°}}$ (left) and $\mathbf{Pt_{30°}/G_{30°}}$ (right), but became disordered after the structural optimization. Nevertheless, the situation for a Pt adlayer on a free-standing graphene differs. The Pt layer is allowed to adsorb on the free-standing graphene sheet in an ordered structure either commensurate with ($\mathbf{Pt_{0°}/G}$; **0°** in $\mathbf{Pt_{0°}}$ indicates the angle relative to the graphene lattice) or rotated by 30° with respect to the graphene lattice ($\mathbf{Pt_{30°}/G}$), as shown in Figure S4(b). The uniformly distributed charges of $\mathbf{Pt_{0°}/G}$ and $\mathbf{Pt_{30°}/G}$ from the top views (the lower part Figure S4(b)) also confirmed that the preferred 0° and 30°

orientations between graphene and Pt layers are constrained by both their lattices as well as charges, the same as that from $\mathbf{G_{0°}}$ and $\mathbf{G_{30°}}$ (Figure 5(a)). The adsorption in either case is weak (-0.19 and -0.10 eV/unit). Such a Pt adlayer-graphene interaction ($\mathbf{Pt_{0°}/G}$ or $\mathbf{Pt_{30°}/G}$) exhibits the feature of a van der Waals interaction and resembles that of $\mathbf{Pt_{0°}/G_{30°}}$.

Figure S5 shows the optimized structures (top and side views) of a series of 3D Pt clusters (Pt_{37}, Pt_{22}, Pt_{10} and Pt_4) on the graphene/Pt(111) substrates, $\mathbf{G_{0°}}$ and $\mathbf{G_{30°}}$. The 3D Pt clusters, graphene layers and top few layers of Pt(111) surface were fully relaxed during the optimization. The results, combining with the calculations with the largest cluster (Pt_{55}), shown in Figure 6(c), were employed to examine the growing Pt clusters on the graphene. The optimized structures show that the Pt clusters have similar shapes on both substrates — they have a fcc phase and grow in (111) orientation; on either $\mathbf{G_{0°}}$ or $\mathbf{G_{30°}}$, their rotational angles relative to the underlying Pt(111) lattice are 0°, like the Pt adlayers (Figure 6(b)). On the other hand, the Pt clusters on $\mathbf{G_{0°}}$ have much stronger adsorption energy and induce further corrugation of the graphene surfaces, whereas the weakly adsorbed Pt clusters on $\mathbf{G_{30°}}$ have greater cluster-graphene distances and rather flat graphene surfaces.

References

1. Gao, M.; Pan, Y.; Huang, L.; Hu, H.; Zhang, L. Z.; Guo, H. M.; Du, S. X.; Gao, H.-J., Epitaxial growth and structural property of graphene on Pt(111). *Applied Physics Letters* **2011,** *98* (3), 033101.
2. Preobrajenski, A. B.; Ng, M. L.; Vinogradov, A. S.; Mårtensson, N., Controlling graphene corrugation on lattice-mismatched substrates. *Physical Review B* **2008,** *78* (7), 073401.

Figure S1

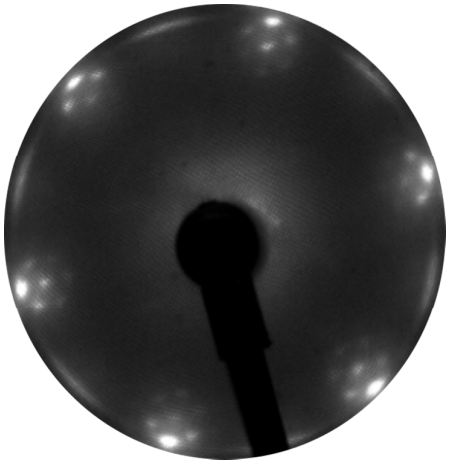
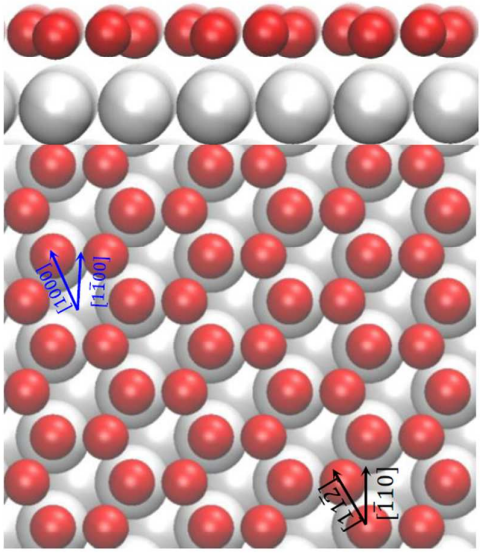


Figure S1 a LEED pattern for a graphene/Pt(111) surface. The graphene was grown on exposing Pt(111) to ethylene (300 L) at 950 K and then annealing the sample at the same temperature for 10 min.

Figure S2

(a)



(b)

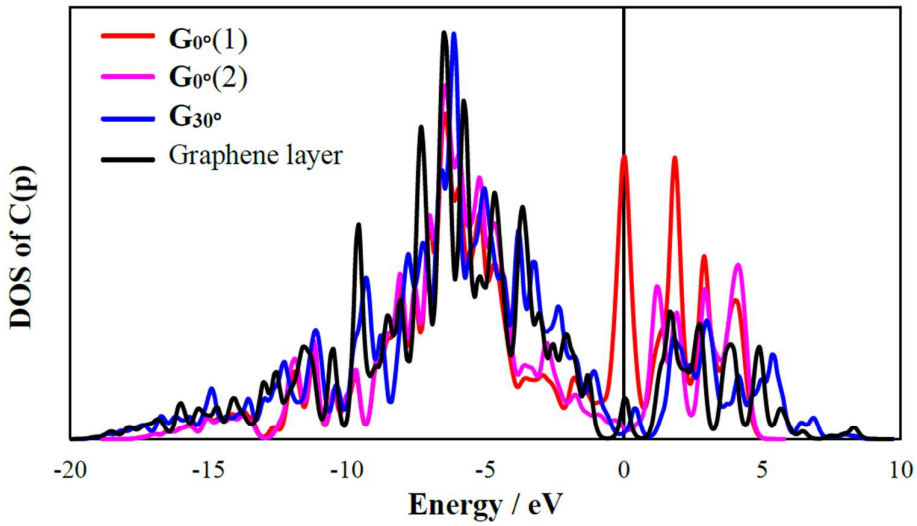


Figure S2. (a) Corrugated graphene sheet of $\mathbf{G_{0°}}$ in the zoom-in top and side views through direction $[1\bar{1}00]$ of the graphene and direction $[\bar{1}10]$ of the Pt(111) surface; (b) DOS analysis for the *p* bands of carbon (C) atoms of the grown graphene

on Pt(111). In (a), the red and grey balls denote C and Pt atoms, respectively; the rotations of adsorbed graphene and the Pt(111) surface are noted with blue and black arrows and numbers, respectively. Two types of C are found in $\mathbf{G_{0°}}$, red ($\mathbf{G_{0°}}$(1)) and purple ($\mathbf{G_{0°}}$(2)) lines, and one type of C was found in $\mathbf{G_{30°}}$, blue line, referenced to that of the isolated graphene layer (black line).

Figure S3

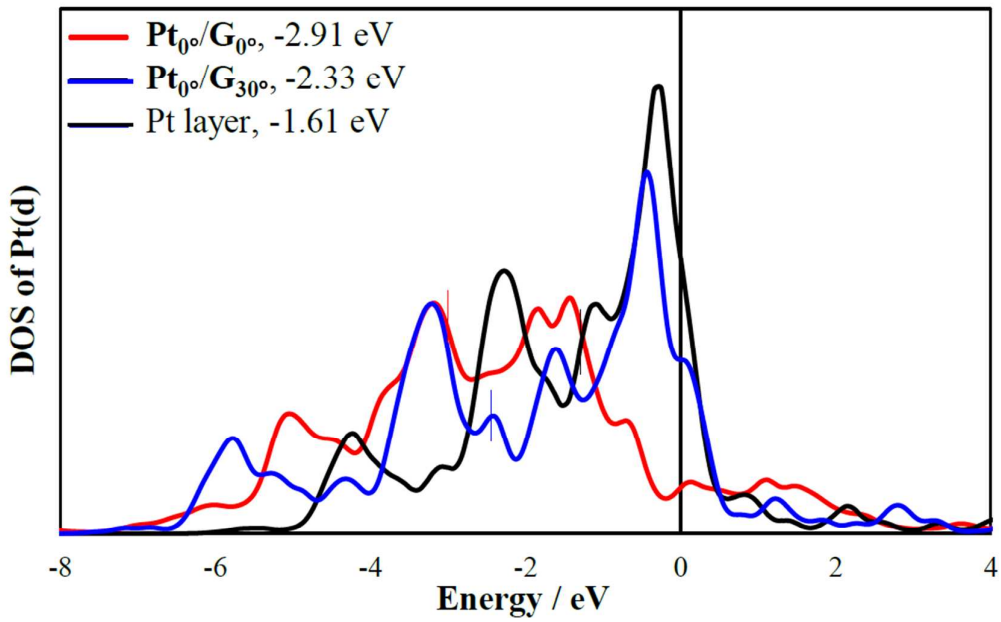
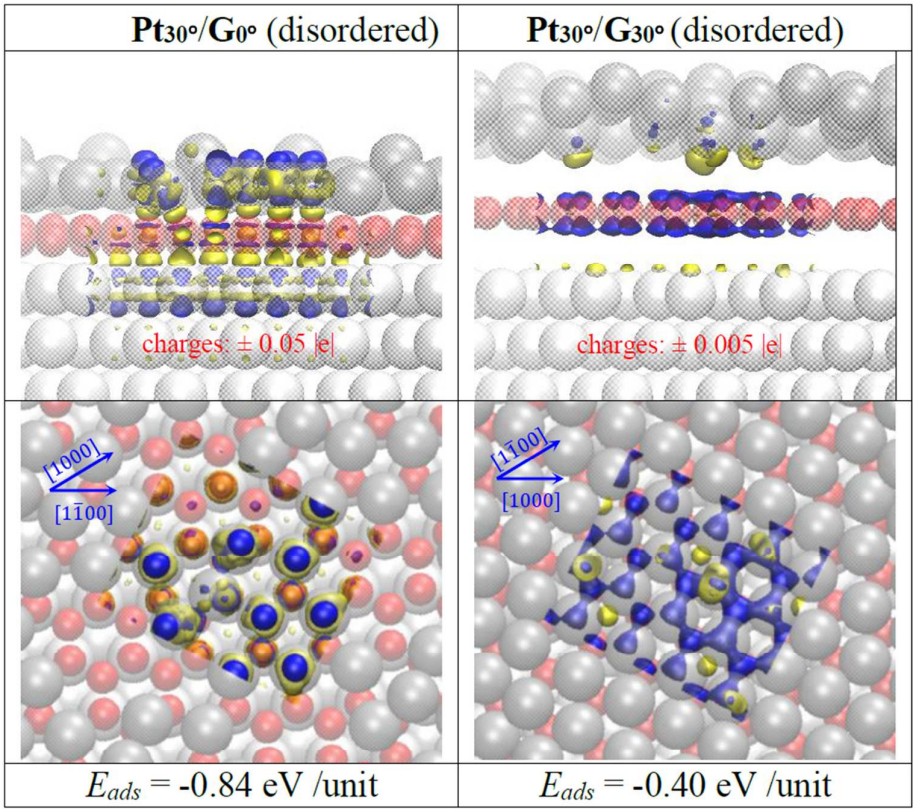


Figure S3. DOS analysis of the *d* bands of the adsorbed Pt layer in **$Pt_{0°}/G_{0°}$** and **$Pt_{0°}/G_{30°}$** is shown in red and blue lines, respectively, referred to that of an isolated Pt layer (black line). Their *d*-band centers are marked with short vertical lines and indicated with numbers in the legend.

Figure S4

(a)



(b)

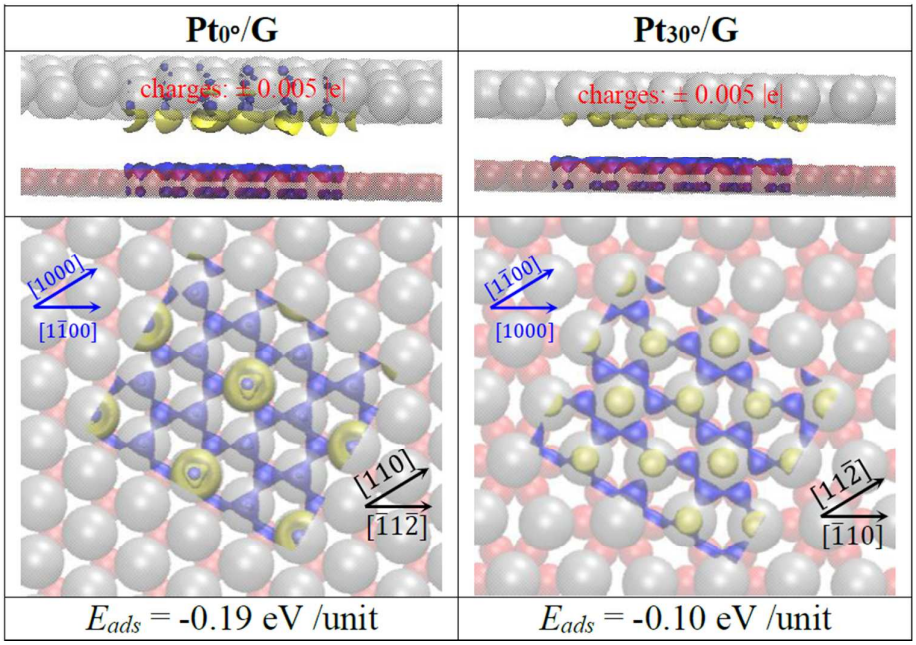


Figure S4. (a) Optimized structures and induced charges of Pt adlayers on the graphene/Pt(111) surfaces. The Pt adlayers were initially set to have a rotation of 30˚

with respect to the beneath Pt lattice, **$Pt_{30°}/G_{0°}$** (left) and **$Pt_{30°}/G_{30°}$** (right), but became disordered after the structural optimization. The orientations of the graphene are noted with blue arrows and numbers. (b) Optimized structures and induced charges of a Pt layer on an isolated graphene sheet. The Pt layer is orderly and uniformly adsorbed in both commensurate and 30º-rotated configurations, **$Pt_{0°}/G$** and **$Pt_{30°}/G$**, respectively. C and Pt atoms are represented with red and white balls, respectively; the orientations of the Pt adlayer and graphene sheet are noted with black and blue, respectively, arrows and numbers. Induced charges are plotted with yellow/blue spheres for +/– 0.05 |*e*| of densely charged **$G_{0°}$** and +/– 0.005 |*e*| of sparsely charged **$G_{30°}$**.

Figure S5

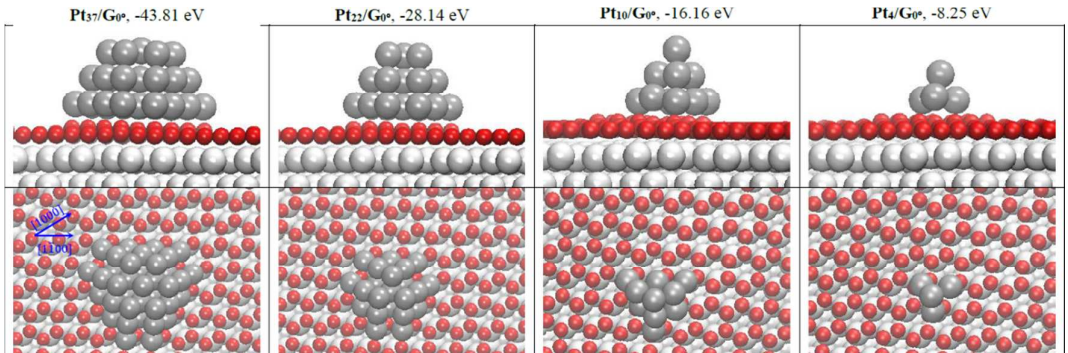


Figure S5. Top and side views of optimized structures and related E_{ads} of 3D Pt clusters, Pt_{37}, Pt_{22}, Pt_{10} and Pt_4 (grey balls), on $\mathbf{G_{0°}}$ and $\mathbf{G_{30°}}$ substrates. The rotations of the beneath Pt(111) surface (white balls) are noted in black arrows and numbers; those of the graphene (red balls) are noted in the blue ones.