Electronic Supplementary Information

Layer-dependent morphologies and charge transfer of Pd on n-layer graphenes

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There are 8 parts in this Electronic Supplementary Information:

1. Graphene sample preparation and characterization
2. The determination of graphene thickness using Raman spectroscopy
3. The typical AFM image of monolayer graphene
4. The EDX spectra of Pd-decorated graphenes
5. The calculation of peak intensity ratio (I_{2D}/I_G)
6. The doping effect of Au and Ag on monolayer graphene
7. The calculation of the electron doping level
8. The varying of Raman parameters with Pd thickness

1. Graphene sample preparation and characterization

The n-layer graphenes were mechanically exfoliated from natural graphite (Alfa Aesar) by using Scotch transparent tape 600 (3M), and then transferred onto the silicon substrate with a 300 nm SiO_2 layer.[1] The layer number of n-layer graphenes was determined using the combined techniques of optical microscope (Leica DM 4000) and micro-Raman spectroscopy (Renishaw inVia Raman Spectroscope) with 514 nm laser excitation.[1] Subsequently, a thin layer of Pd film was thermally evaporated onto the silicon wafer in a vacuum thermal evaporator at a deposition rate of 1.0 Å/s under a vacuum of ~ 10^{-4} Pa, which was then characterized by scanning electron microscopy (SEM) and Raman spectroscopy.

The micro-Raman spectroscopy (Renishaw inVia Raman Spectroscope) experiments were carried out under ambient conditions with 514.5 nm (2.41 eV) excitation from an argon ion laser. The laser power on the sample was set at around 1.0 mW to avoid laser induced heating. The application of a 100× objective lens with a numerical aperture of 0.90 can provide us a ~ 1 μm laser spot size. Several Raman spectra (~ 10) of pristine or Pd-decorated n-layer graphenes were collected to ensure the credibility and repeatability of the results.

2. The determination of graphene thickness using Raman spectroscopy

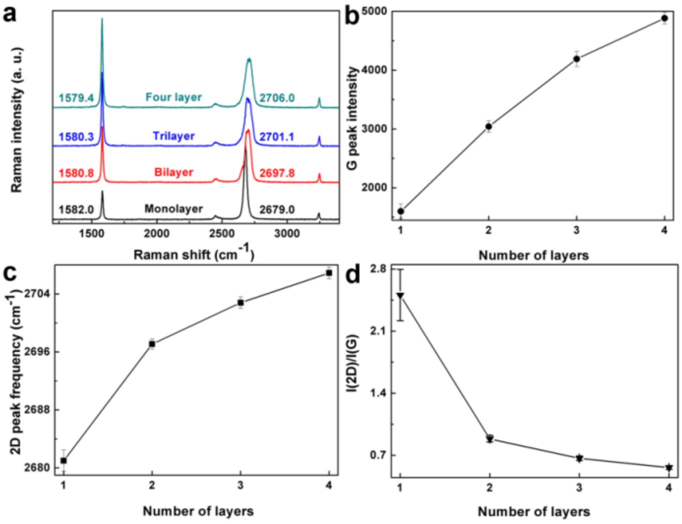


Fig. S1. The Raman spectra (a), G peak intensity (b), 2D peak frequency (c) and peak intensity ratio (d) of pristine n-layer graphenes (n = 1, 2, 3, 4), which are obviously dependent on the layer number of n-layer graphenes.

3. The typical AFM image of monolayer grapheme

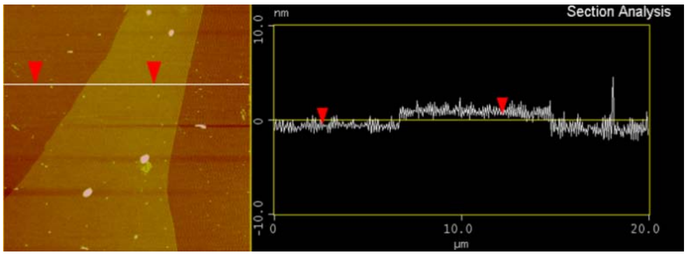
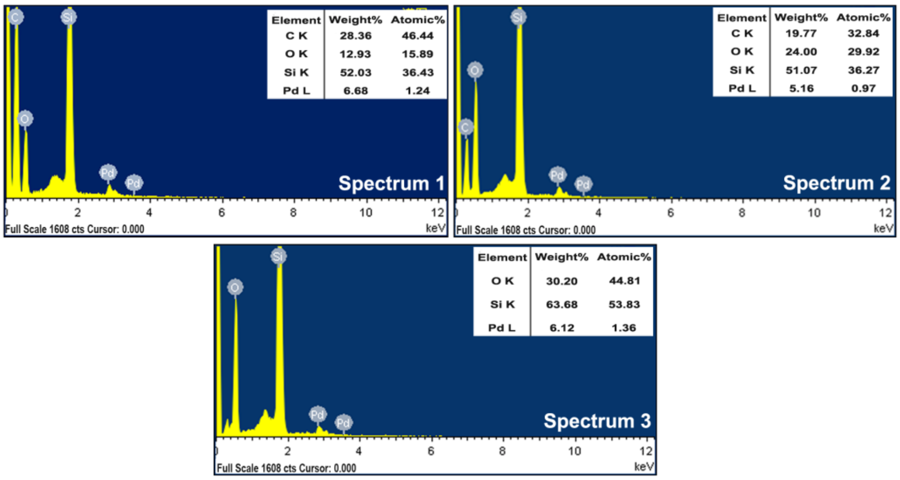


Fig. S2. The typical AFM image of monolayer graphene.

AFM technique has been applied to characterize the thickness of monolayer graphene, which is shown in Fig. S2. This AFM image is measured in a size of 20 × 20 μm^2. From the right curve of the thickness, we can determine the thickness of monolayer graphene is around 0.8 - 1.0 nm, which is in accordance with previously reported results.[2]

4. The EDX spectra of Pd-decorated graphenes



Element	Weight%	Atomic%
C K	28.36	46.44
O K	12.93	15.89
Si K	52.03	36.43
Pd L	6.68	1.24

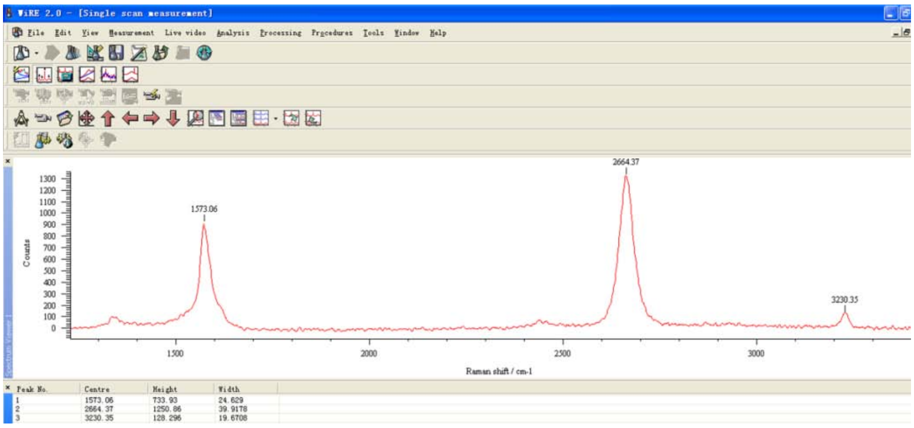
Element	Weight%	Atomic%
C K	19.77	32.84
O K	24.00	29.92
Si K	51.07	36.27
Pd L	5.16	0.97

Element	Weight%	Atomic%
O K	30.20	44.81
Si K	63.68	53.83
Pd L	6.12	1.36

Fig. S3. EDX spectra showing the obvious Pd signals on thick, thin graphene, and substrate. Spectrum 1, 2 and 3 corresponds to EDX on the thick, thin graphene and the substrate, respectively.

5. The calculation of peak intensity ratio (I_{2D}/I_G)

The Raman spectroscopy-provided software “Renishaw wire 2.0” can give us the following detailed information: peak frequency, peak intensity and full width at half maximum. Thus, the peak intensity ratio can be calculated from 2D peak intensity divided by that of G peak. For example, in this spectrum, $I_{2D} = 1250.86$ counts, $I_G = 733.93$ counts, we can get the intensity ratio $I_{2D}/I_G = 1250.86/733.93 \approx 1.7$.



Peak No.	Centre	Height	Width
1	1573.06	733.93	24.629
2	2664.37	1250.86	39.9178
3	3230.35	128.296	19.6708

Fig. 4 The parameters of Raman spectrum of Pd-decorated monolayer grapheme given by the software of Raman spectroscopy.

6. The doping effect of Au and Ag on monolayer graphene

After 2 nm Ag deposition, for monolayer graphene, the G peak shifts to the lower frequency (red Raman shift). However, after 2 nm Au deposition, the G peak shifts to the higher frequency (blue Raman shift). Meanwhile, the full width at half maximum of G and 2D peaks become much larger after Au and Ag deposition.

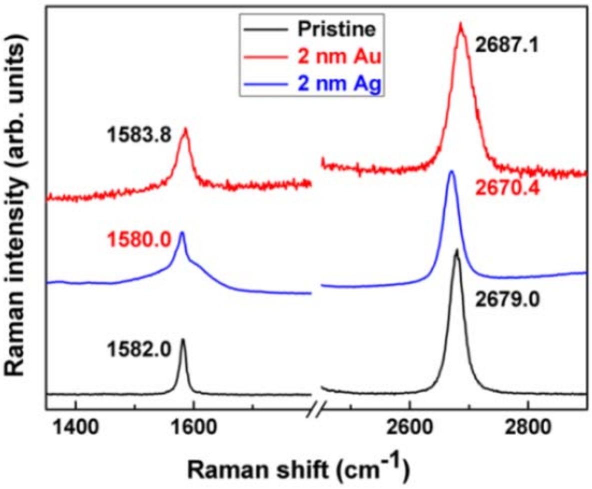


Fig. S5. The frequency shift of G peak in Raman spectra of 2 nm Au or Ag-decorated monolayer graphene.

7. The calculation of the electron doping level

Previously reported results[3] show that the Fermi energy in graphene changes as $E_F(n) = \frac{h}{2\pi} \times | V_F | \sqrt{\pi n}$, and the relationship between top-gate voltage and carrier concentration can be described by the following equation: $V_{TG}(\text{volts}) = \frac{E_F}{e} + \frac{ne}{C_{TG}}$, where $| V_f | = 1.1 \times 10^6$ ms^{-1}, $C_{TG} = 2.2 \times 10^{-6}$ F cm^{-2}. Thus, $V_{TG}(\text{volts}) = 1.16 \times 10^{-7} \times n^{1/2} + 0.723 \times 10^{-13} \times n$, where n is the carrier or electron concentration.

After 0.5 nm Pd decoration, red Raman shift of G peak is around 8.4 cm^{-1}. According to the top-gate modulated G peak position varying with electron concentration,[3] Raman shifts of G peak (~ 8.4 cm^{-1}) is equivalent to about 8.4×10^{12} cm^{-2} electron concentration, and top-gate voltage ~ 0.94 V. Thus, the Dirac point moves to the conduction band for about 336 meV.

8. The varying of Raman parameters with Pd thickness

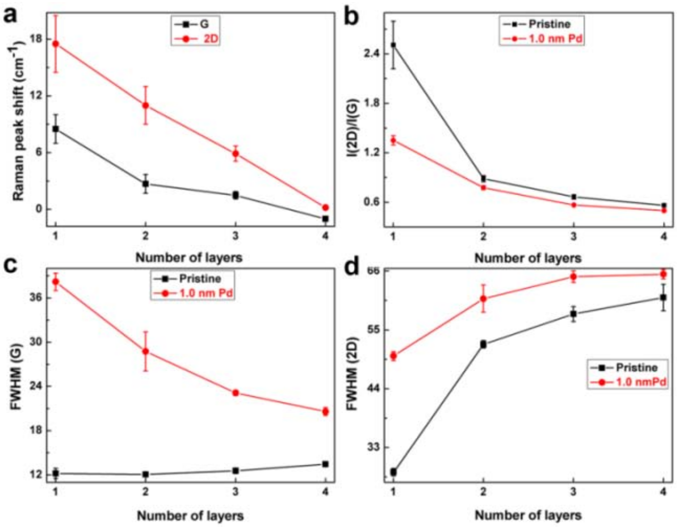


Fig. S6. The peak frequency shifts, intensity ratio (I_{2D}/I_G) and full width at half maximums of G and 2D peaks in Raman spectra of 1.0 nm Pd-decorated n-layer graphenes compared with pristine graphenes.

After 1.0 or 1.6 nm Pd film deposition onto n-layer graphenes, according to the Raman measurements at 514 nm laser excitation, similar to the situation of 0.5 nm Pd deposition, Raman shifts of G and 2D peaks are also dependent on the layer number, which are shown in Fig. S6 or S7.

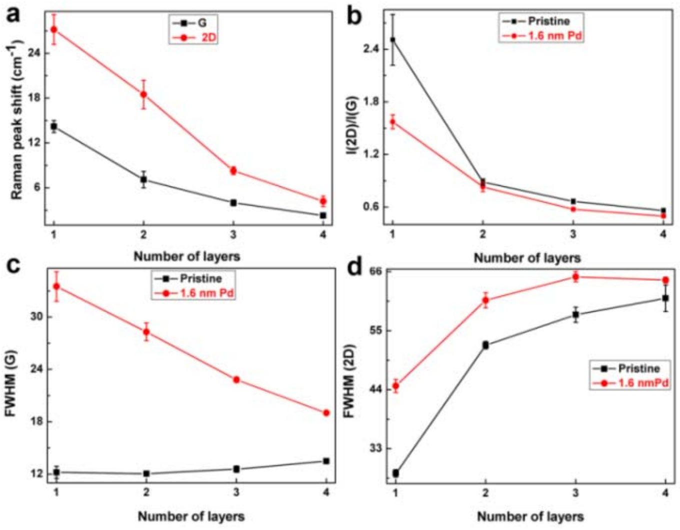


Fig. S7. The peak frequency shifts, intensity ratio (I_{2D}/I_G) and full width at half maximums of G and 2D peaks in Raman spectra of 1.6 nm Pd-decorated n-layer graphenes compared with pristine graphenes.

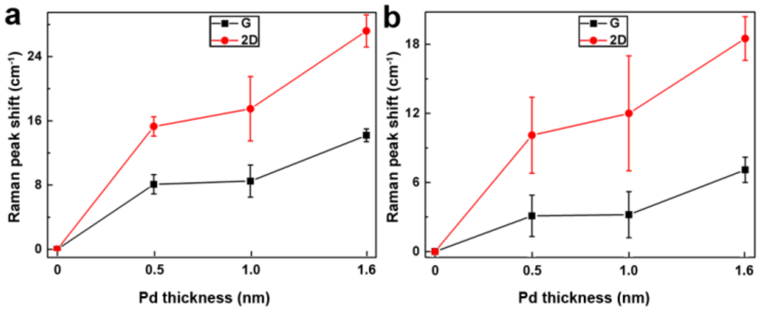


Fig. S8. The effects of Pd film thickness on charge transfer between graphenes and Pd. (a) Monolayer and (b) bilayer graphene.

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