Electronic Supplementary Information

The structure and properties of graphene on gold nanoparticles

Zoltán Osváth[1,3], András Deák[1], Krisztián Kertész[1,3], György Molnár[1], Gábor Vértesy[1], Dániel Zámbó[1], Chanyong Hwang[2,3], and László Péter Biró[1,3]

[1] Institute of Technical Physics and Materials Science, MFA, Centre for Energy Research, HAS, 1525 Budapest, P.O. Box 49, Hungary, www.nanotechnology.hu

[2] Center for Nano-metrology, Division of Industrial Metrology, Korea Research Institute of Standards and Science, Yuseong, Daejeon 305-340, Republic of Korea

[3] Korea-Hungary Joint Laboratory for Nanosciences (KHJLN), P.O. Box 49, 1525 Budapest, Hungary

Graphene grown by chemical vapour deposition (CVD) was transferred onto Au(5 nm)/SiO_2 substrate and annealed at 400 ^{o}C in Ar atmosphere for 2 hours. The sample was characterized by tapping mode atomic force microscopy (AFM). Figure S1 shows a crumpled graphene sheet supported on gold nanoparticles (Au NPs). The corrugation of this particular graphene sheet is dominated by star-shaped rippling developed around individual nanoparticles. Note, that the amplitude of wrinkling can reach 5–10 nm (height profile 2). However, by comparing the height profiles 1 and 2, we find that even the highly crumpled graphene parts remain completely detached from the underlying SiO_2 surface.

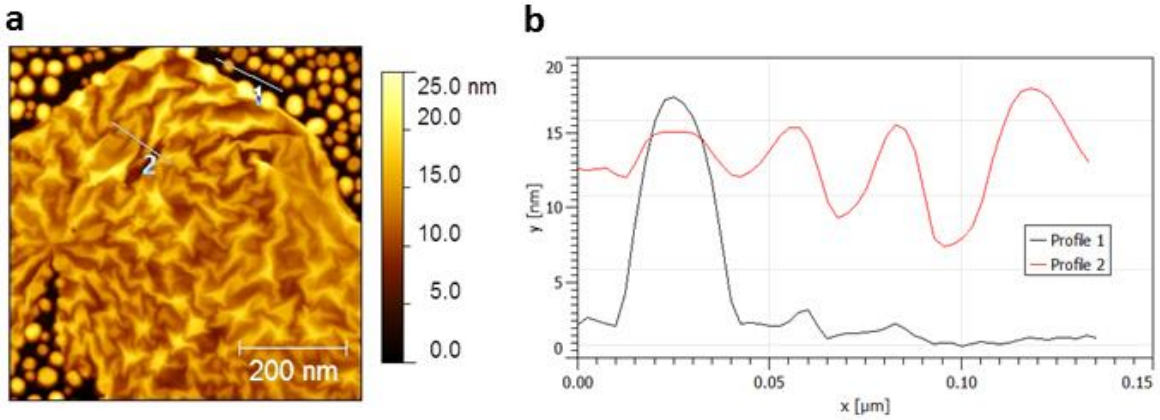

Figure S1. *(a) Tapping mode AFM image of graphene on gold nanoparticles. The height profiles corresponding to the line section 1 and 2 are shown in (b).*

Confocal Raman spectroscopy was performed on graphene/Au NPs both before and after annealing at 500 ^{o}C in N_2 atmosphere. Reference spectra from graphene/SiO_2 were recorded on areas not covered by Au NPs of the same sample. Figure S2 shows correlation plots constructed from the G and 2D graphene peak positions (ω_G, ω_{2D}) acquired from areas of 5×5 µm^2. Figure S2a and S2c show correlation plots obtained with excitation laser 488 nm, before and after annealing, respectively. Similarly, Figure S2b and S2d display correlation plots corresponding to measurements performed with a laser of 633 nm, before and after annealing, respectively. We plotted the slope $\frac{\Delta\omega_{2D}}{\Delta\omega_G} = 2.2$ corresponding to variations induced by strain only (solid line), and the slope $\frac{\Delta\omega_{2D}}{\Delta\omega_G} = 0.75$ corresponding to p-type doping [1] (dotted line). The equilibrium values $(\omega_G^0, \omega_{2D}^0)$ are taken as $(1581\ cm^{-1}, 2691\ cm^{-1})$ and $(1581\ cm^{-1}, 2635\ cm^{-1})$ for 488 and 633 nm laser, respectively.

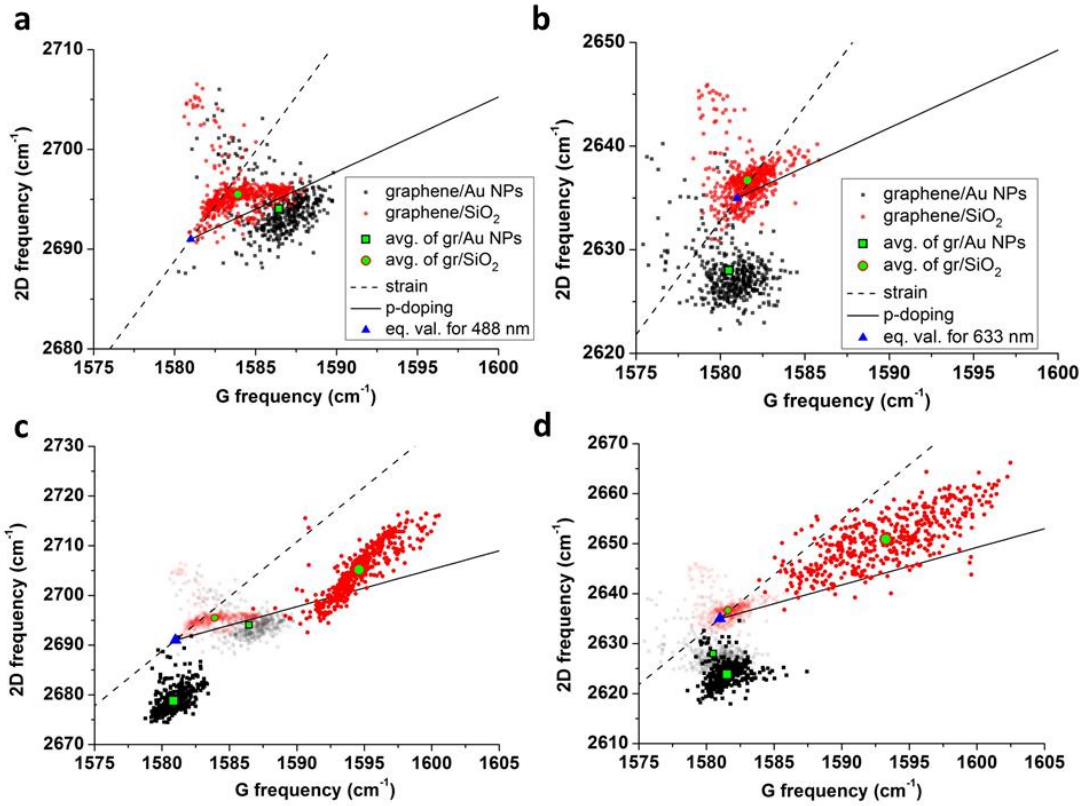

Figure S2. *(ω_G, ω_{2D}) correlation plots constructed from measurements areas of 5×5 μm^2. The corresponding average peak positions are marked with green symbols. The equilibrium values for 488 nm (and 633 nm) laser are shown with blue triangles. The slopes denoting purely strain (straight line) and purely doping effects (dashed line) are also plotted. Red dots denote measurements on graphene/SiO_2, while black dots correspond to measurements on graphene/Au NPs. The measurements performed before annealing are shown in a) for 488 nm laser and b) for 633 nm laser. Data after annealing are displayed in c) for 488 nm laser and d) for 633 nm laser. As guide for the eye, in Figure c) and d) the same data as in a) and b) is also re-plotted in a semi-transparent style.*

For the 488 nm laser (Figure S2a) the distribution of peaks corresponding to graphene/Au NPs partially overlap with the data from graphene/SiO_2. In the former case the average values for the G and 2D peaks are $(1586.4\, cm^{-1}, 2694\, cm^{-1})$, while in the latter case these averages are $(1583.9\, cm^{-1}, 2695.5\, cm^{-1})$. Interestingly, when the same areas are measured with 633 nm laser (Figure S2b), the two distributions are more separated from each other, with average peak positions $(1580.5\, cm^{-1}, 2628\, cm^{-1})$ for graphene/Au NPs and

($1581.6\ cm^{-1}, 2636.7\ cm^{-1}$) for graphene/$SiO_2$. We consider the difference between average 2D peak positions ($\Delta\omega_{2D}$), which is more significant. Note that this difference is only $-1.5\ cm^{-1}$ for 488 nm laser, while for 633 nm $\Delta\omega_{2D} = -8.7\ cm^{-1}$. Since we measured the same areas of 5×5 μm^2, we presume that the strain in graphene is the same for the two cases. This means that the larger difference $\Delta\omega_{2D}$ measured with 633 nm laser should be ascribed to doping effects. This laser wavelength is closer to the surface plasmon resonance (SPR) of gold nanoparticles (see also the main text). Close to the SPR, more plasmons are excited and larger number of hot electrons can be injected into graphene [2, 3]. The results indicate that the dynamic doping of graphene on Au NPs is more significant when irradiated with 633 nm laser. After annealing (Figure S2c-d), the peak positions are distributed mainly along a direction parallel to the strain slope, showing that strain is induced by the annealing process. Compressive strain is induced in graphene/SiO_2, with (ω_G, ω_{2D}) values larger than the equilibrium values (red dots), while a small tensile strain develops in graphene/Au NPs (black dots). We can estimate this tensile strain (ε) using $\varepsilon = -(\omega_{2D}^{avg} - \omega_{2D}^{o})/(2\omega_{2D}^{o}\gamma_{2D})$ [4], with $\gamma_{2D} = 2.7$ the Grüneisen parameter of the 2D peak obtained from first-principles calculations [5]. The average of 2D peak positions after annealing is $\omega_{2D}^{avg} = 2678.8\ cm^{-1}$ (with 488 nm laser), which yields a strain of $\varepsilon = 0.084$ %.

Optical reflectance spectra of graphene/Au NPs/SiO_2 measured under perpendicular illumination and detection angle of 15^o are shown in Figure S3a. The minimum of the spectrum measured before annealing (black line) is red-shifted compared to the surface plasmon resonance (SPR) of the Au NPs/SiO_2 (dotted line), while after annealing (red line) the spectrum is blue-shifted compared to the SPR. The reference spectrum of graphene/SiO_2 is also displayed (dashed line).

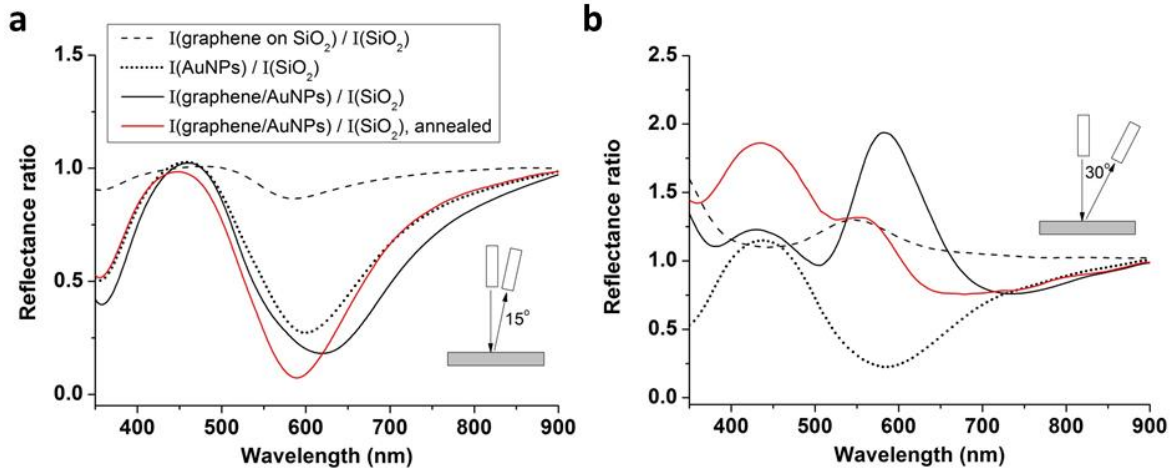

Figure S3. *Optical reflectance spectra of graphene samples. All spectra are divided by the spectrum recorded from bare SiO_2 surface. The spectra of graphene/Au NPs are shown before and after annealing, with black and red solid lines, respectively. For reference, the spectra of graphene/SiO_2 and Au NPs/SiO_2 are also displayed with dashed and dotted lines, respectively. a) Reflectance spectra measured under perpendicular illumination and detection angle of 15^o. b) Reflectance measurements under perpendicular illumination and detection angle of 30^o.*

Interestingly, the reflection characteristics are different for detection angle of 30^o (Figure S3b). Significant light is scattered at this angle, near the SPR (black line), and the shape of the reflectance changes considerably after annealing (red line).

The extinction cross section of a single dome-like nanoparticle was simulated using COMSOL Multiphysics®, based on the modification of a readily available COMSOL model (Model ID: 14443). For the gold dome, the dielectric data from Johnson and Christy [6] was interpolated for each simulated wavelength. For the supporting oxide layer the refractive index of n=1.45, and for Si the built-in parameters were used. The simulation yields a SPR at 590 nm (Figure S4), in good agreement with the resonance wavelength obtained from optical reflectance spectra (597 nm).

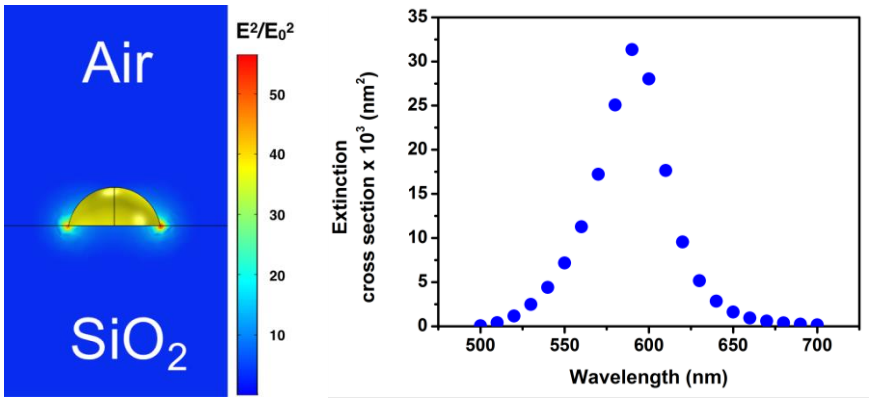

Figure S4. *Simulated structure with near-field map at resonance (590nm) excitation (left) and extinction spectrum (right) of a single Au dome on a Si/SiO_2 (285 nm) substrate. Dome diameter at the substrate: 46 nm; dome height: 19 nm. Light polarization parallel to the slice plane.*

References

[1] J. E. Lee, G. Ahn, J. Shim, Y. S. Lee and S. Ryu, *Nat. Commun.* 2012, **3**, 1024.

[2] Z. Fang, Y. Wang, Z. Liu, A. Schlather, P. M. Ajayan, F. H. L. Koppens, P. Nordlander and N. J. Halas, *ACS Nano* 2012, **6**, 10222.

[3] A. Hoggard, L. Wang, L. Ma, Y. Fang, G. You, J. Olson and Z. Liu, *ACS Nano* 2013, **7**, 11209.

[4] F. Ding, H. Ji, Y. Chen, A. Herklotz, K. Dörr, Y. Mei, A. Rastelli and O. G. Schmidt, *Nano Lett.* 2010, **10**, 3453.

[5] T. Mohiuddin, A. Lombardo, R. Nair, A. Bonetti, G. Savini, R. Jalil, N. Bonini, D. Basko, C. Galiotis, N. Marzari, K. Novoselov, A. Geim and A. Ferrari, *Phys. Rev. B* 2009, **79**, 205433.

[6] P. B. Johnson and R. W. Christy, *Phys. Rev. B* 1972, **6**, 4370.