Electronic Supplementary Information

for

Effects of surface roughness of Ag thin films on surface-enhanced Raman spectroscopy of graphene: spatial nonlocality and physisorption strain

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1. Reasons for relative low SERS enhancement factor

The enhancement factor is determined by a few of factors, including the localization level of surface plasmons, the density of hot spots, and the spectral difference between the excitation laser wavelength and the plasmon resonance wavelength.

First, the resonant wavelength of surface plasmon is around 330 nm in our structure, and the excitation wavelength in our Raman system is 488 nm. Hence, the large difference between the resonance wavelength and the excitation wavelength decrease the enhancement factor greatly.

Second, the localization level in our structure is not that high. Using the conventional overlapped semi-cylinder model, we can compare our results with that reported in Phys. Rev. Lett. 77 (1996) 1163. In the PRL paper, the structure of $r = 15$ nm and $D = 2.4r$ (D: distance between the outside edges of two neighboring grains, and r: the radii of the cylinders) has the enhancement factor around $10^2$ at 488 nm. In our structure of $r = 85.24$ nm and $D = 2r$, the large radii can induce few hot spots in the same Raman collection volume. Combined with difference between excitation and resonance wavelength, the enhancement factor about 20–30 at 488 nm is reasonable. This experimental result agrees well with our theoretical calculation, as shown in Figure 3.

2. Local surface temperature effect on the red-shift

The local surface temperature induced by surface plasmons is dependent on the density of hot spots, the thermal conductivity of the underlying materials, the laser exposure time, the enhancement factor, and the difference between the excited wavelength and the resonance wavelength. Nguyen et al. reported the temperature-dependent red-shift Raman peak of graphene (-0.05 cm$^{-1}$/K). Donner et
al. and Baffou et al. reported the methods to mapping the temperature of Au particles.\textsuperscript{4,5} The Au nanoparticles lay on thermally-isolating glass substrate. The excitation laser wavelength is 850 nm, which is in resonance with the plasmonic structure. The temperature of Au particles is beneath 100 °C in the work. Compared with our structure, the Ag rough thin film is 100 nm thick and the area is 1 cm\textsuperscript{2}. The excitation laser wavelength (488 nm) is far away from resonant wavelength (~330 nm) of rough Ag films. The heat generation by the plasmonic enhancement is relative limited compared to other works.\textsuperscript{4,5} In addition, our structure is continuous Ag film instead of isolated Ag nanoparticles. The underlying Ag thin film has high thermal conductivity (429 W·m\textsuperscript{-1}·K\textsuperscript{-1}), and can dissipate the generated heat quickly. So we infer that 10 cm\textsuperscript{-1} Raman red-shift (equivalent to the temperature rise of 200 °C) cannot be attributed to the local surface temperature of different roughness Ag films.

It is hard to measure nanoscale temperature on Ag surface. If the local surface temperature is high enough to affect the peak position shift in Raman spectrum of graphene, the temperature-induce red-shift effect can be magnified by prolonging the laser exposure time. Fig. S1 shows the time evolution of the Raman spectra of graphene on rough Ag film during 10-min laser exposure. We find no obvious red-shift in the Raman spectra of graphene. So we conclude that temperature is not the major reason to induce the observed Raman peak shift of graphene in our structure.

![Fig. S1. Time evolution of 2D Raman peak of graphene on the rough Ag films for 10- min laser exposure.](image-url)
References


