Infrared fingerprint spectroscopy of nanoscale molecules with graphene plasmons

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1. Extended Abstract

Far-field mid-infrared (MIR) spectroscopy has an increasingly important role for numerous applications (for example, chemical detection, food safety and biosensing) through directly probing vibrational characteristics of a broad range of molecular species and compounds. In particular, in the molecular fingerprint region from 600 to 1500 cm^{-1} (corresponds to the wavelength range of 6–16 μm), complex vibrational characteristics of molecules in bulk materials can be effectively distinguished to enable unambiguous identification of molecular structures and species. However, molecular fingerprinting at the nanoscale level still remains a significant challenge (as the black line in Figure 1b), due to weak light‑matter interaction between micron-wavelengthed infrared light and nano-sized molecules. We demonstrate molecular fingerprinting at the nanoscale level using our specially designed graphene plasmonic structure on CaF_2 nanofilm, as shown in Figure 1a. This structure not only avoids the plasmon‑phonon hybridization, but also provides in situ electrically-tunable graphene plasmon covering the entire molecular fingerprint region, which was previously unattainable.[1] We enhance about 8-nm PEO film vibrational signatures up to larger than 20-fold (Figure 1b). In addition, undisturbed and highly confined graphene plasmon offers simultaneous detection of in-plane and out-of-plane vibrational modes with ultrahigh detection sensitivity down to the sub-monolayer level, significantly pushing the current detection limit of far-field mid-infrared spectroscopies. Our results provide a platform, fulfilling the long-awaited expectation of high sensitivity and selectivity far-field fingerprint detection of nano-scale molecules for numerous applications.

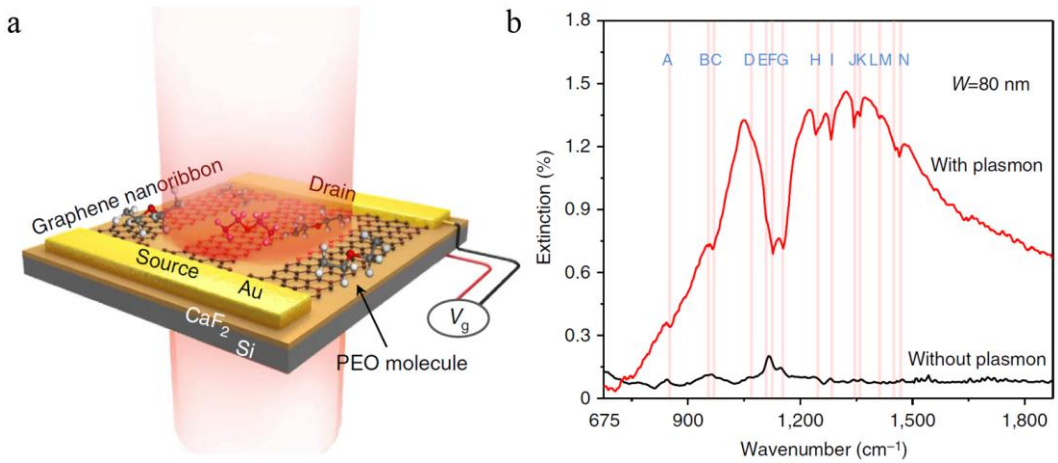

Figure 1. (a) Schematic of the graphene plasmon-based sensor. Graphene nanostructure was designed on 300 nm-thick CaF_2 film. Graphene plasmon excited by the incident infrared beam (the red shaded pillar) can be tuned *in situ* by gate voltage (V_g). (b) A comparison of the sensing results for an 8-nm-thick PEO film with and without graphene plasmon enhancement. Graphene Fermi level is about 0.2 eV. The vertical lines indicate PEO molecular vibrational modes in the as-shown region.

2. References

1. H. Hu, X. X. Yang, F. Zhai, D. B. Hu, R. N. Liu, K. H. Liu, Z. P. Sun and Q. Dai, "Far-field nanoscale infrared spectroscopy of vibrational fingerprints of molecules with graphene plasmons," *Nature Communications*, **7**, 12334, July 2016, pp. 1-8, doi: 10.1038/ncomms12334.