BIOMECULAR SURFACE-ENHANCED RAMAN SPECTROSCOPY

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Surface-enhanced Raman spectroscopy (SERS) is widely employed and promising spectroscopy technique for physicochemical analysis and sensing of biomolecules. Advances in plasmonic substrates nanotechnology boosted Raman signal up to 108 times and provided opportunity for single molecule detection. However, biomedical applications of SERS technique is hindered by the lack of signal repeatability and quantification. The heterogeneity of rough metal substrates, presence of hot spots, degradation of surface structures and diverse metal-adsorbate interactions are mainly responsible for the irreproducibility of SERS spectra. To overcome these limitations, two extraordinary Raman techniques related with signal amplification were developed in 2010. Tian et al., developed shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS) and Ling et al., reported graphene-enhanced Raman scattering (GERS) effect [1]. Flat graphene surface produces repeatable and strong GERS spectra from organic molecules able chemically interact with the substrate (chemical enhancement mechanism).

Recently, we have compared GERS and SHINERS approaches for probing structure of adsorbed riboflavin Rf [2]. Rf or vitamin B2 is a water-soluble vitamin that plays an essential role in cellular biochemistry. Relative intensity of 2D and G bands reveals presence of single-monolayer graphene substrate (Figure 1). Upon adsorption of Rf, GERS bands are visible at 1351, 1411, and 1536 cm−1. We found that in SHINERS spectrum intensity of Rf bands increases by a factor of 26. In addition, more detailed vibrational spectrum of biomolecule was observed. We have demonstrated that SHINERS spectroscopy has a great potential to probe absorbed biomolecules at graphene.

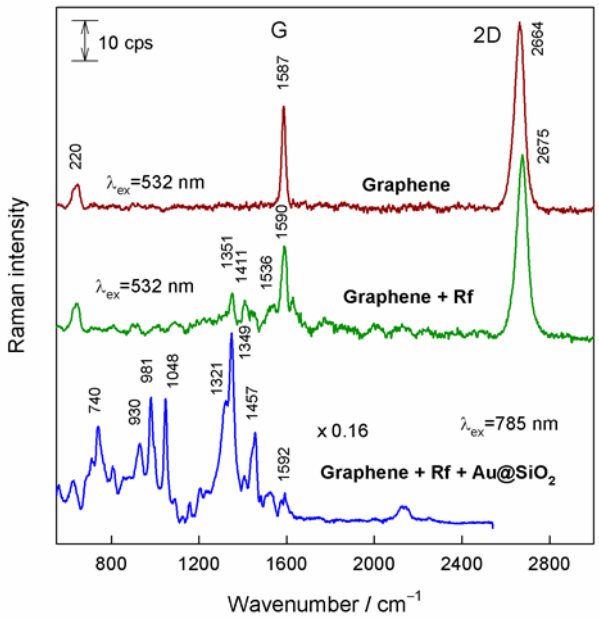

Figure 1. Resonance Raman spectra of graphene and graphene with adsorbed riboflavin (Rf) observed with 532 nm excitation wavelength and SHINERS spectrum of Rf adsorbed on graphene with Au@SiO2 nanoparticles observed with 785 nm excitation wavelength.

References

1. N. Zhang, L. Tong, J. Zhang, Chem. Mater. 28, 6426 (2016).
2. A. Zdaniauskienė, I. Ignatjev, T. Charkova, M. Talaikis, A. Lukša, A. Šetkus, G. Niaura, Materials 15, (2022) (in press).