Molecular sensitivity and selectivity of metal nanoparticles decorated graphene as 'smart' surface-enhanced Raman scattering (SERS) platforms

A. Banaszak, T. Smith and Sanju Gupta

Department of Physics and Astronomy, Western Kentucky University, Bowling Green, KY 42101

Raman scattering signal enhancement that uses graphene as support, graphene-enhanced Raman scattering (GERS), is a recent phenomenon. It can produce clean and reproducible Raman signals of chemical molecules with significantly enhanced signal intensity in contrast to traditional surface- (SERS) and tip- enhanced Raman scattering (TERS) techniques. While enhancement in SERS and TERS arise due to the electromagnetic mechanism, GERS also relies on a chemical mechanism and therefore shows unique molecular sensitivity and selectivity. In this work, we developed graphene materials decorated with noble metal (silver and gold) nanoparticles for detection of different chemical molecules *e.g.* methylene blue (MB) and rhodamine 6G (Rh6G) keeping in view of their optical and biological importance. The results illustrate that silver and gold nanoparticles immobilized on graphene and its derivatives (graphene oxide and reduced graphene oxide) significantly enhance the signal, in general, and as cascaded amplification of SERS signal on multilayer architecture, in particular, larger than those on the metal nanoparticles in absence of graphene. Additionally, the sensitivity can be tuned by controlling the size of nanoparticles and the highest SERS enhancement factor of almost three to four orders of magnitude is achieved at the optimal 30 nm silver and 40 nm gold nanoparticles on reduced graphene oxide. Moreover, these highly-sensitive graphene-nanoparticle sensors are capable of detecting MB and Rh6G molecules over a broad range of concentration ranging 10 pM to 100 μM. Therefore, these substrates are promising as advanced 'smart' SERS platforms for detection of chemicals with ultrasensitivity. The GERS enhancement is discussed in terms of 1. molecular structures (molecular symmetry; face-down and edge-on and substituents similar to graphene), 2. charge-transfer interaction between molecules and graphene and 3. graphene-metal nanoparticle interfacial hybridization. They are found to be favorable for Raman signal enhancement and corroborated with UV–vis absorption spectra of molecules in contact with or in presence of graphene helping to guide molecular detection useful in medicine and biotechnology.