Excitation-Tunable Gap-Mode TERS from 2D Semiconductors

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Resonant excitation is well-known to enhance SERS/TERS scattering from analytes ranging from molecules to 3D materials. Here, we investigate the dependance of TERS scattering from mono- and bi-layers of WS_2 and MoS_2 in intimate contact with silver on the excitation laser wavelength (within 473nm-830nm spectral range). This is achieved by collecting the TERS maps of the same area featuring both the mono-and the bi-layers with the same probe at six different excitation wavelengths. We found that the response from the mono- and bilayers is very different: the ratio of the A'/A_{1g} peaks that represent similar out-of-plane Raman mode for the mono- and the bi-layer correspondingly, features a sharp dip at A exciton for both MoS_2 and especially for WS_2 (existing laser set matched the excitonic bands in WS_2 particularly well). For the latter material the 632.8nm excitation is very close to A exciton (~620nm) and consequently, TERS response from the monolayers obtained with this most popular laser wavelength for TERS measurements, was dramatically decreased compared to excitation at 671nm and 594nm, making the resonant excitation counterproductive. We propose that this phenomenon arises from intermediate (Fano resonance) or strong coupling (Rabi splitting) between the A exciton in WS_2(MoS_2) and the junction plasmon. This is akin to the so-called Fano(Rabi) transparency experimentally observed in far field (coherent) scattering from transition metal dichalcogenides between two plasmonic metals. Naturally, TERS provides direct control of the gap plasmon, and in turn exciton-plasmon coupling, compared to the rigid geometries that were previously employed in diffraction limited measurements. In effect, our observed phenomenon opens new frontiers for the varied excitation gap-mode TERS as the platform to study fascinating quantum phenomena in systems with intermediate-to-strong coupling between excitons and plasmons in ambient conditions.