Tip-Enhanced Raman Spectroscopy with Plasmonic Lens Focused Longitudinal Electric Field Excitation

Authors : Mingqian Zhang

Abstract : Tip-enhanced Raman spectroscopy (TERS) is a scanning probe technique for individual objects and structured surfaces investigation that provides a wealth of enhanced spectral information with nanoscale spatial resolution and high detection sensitivity. It has become a powerful and promising chemical and physical information detection method in the nanometer scale. The TERS technique uses a sharp metallic tip regulated in the near-field of a sample surface, which is illuminated with a certain incident beam meeting the excitation conditions of the wave-vector matching. The local electric field, and, consequently, the Raman scattering, from the sample in the vicinity of the tip apex are both greatly tip-enhanced owning to the excitation of localized surface plasmons and the lightning-rod effect. Typically, a TERS setup is composed of a scanning probe microscope, excitation and collection optical configurations, and a Raman spectroscope. In the illumination configuration, an objective lens or a parabolic mirror is always used as the most important component, in order to focus the incident beam on the tip apex for excitation. In this research, a novel TERS setup was built up by introducing a plasmonic lens to the excitation optics as a focusing device. A plasmonic lens with symmetry breaking semi-annular slits corrugated on gold film was designed for the purpose of generating concentrated sub-wavelength light spots with strong longitudinal electric field. Compared to conventional far-field optical components, the designed plasmonic lens not only focuses an incident beam to a sub-wavelength light spot, but also realizes a strong z-component that dominants the electric field illumination, which is ideal for the excitation of tip-enhancement. Therefore, using a PL in the illumination configuration of TERS contributes to improve the detection sensitivity by both reducing the far-field background and effectively exciting the localized electric field enhancement. The FDTD method was employed to investigate the optical near-field distribution resulting from the light-nanostructure interaction. And the optical field distribution was characterized using an scattering-type scanning near-field optical microscope to demonstrate the focusing performance of the lens. The experimental result is in agreement with the theoretically calculated one. It verifies the focusing performance of the plasmonic lens. The optical field distribution shows a bright elliptic spot in the lens center and several arc-like side-lobes on both sides. After the focusing performance was experimentally verified, the designed plasmonic lens was used as a focusing component in the excitation configuration of TERS setup to concentrate incident energy and generate a longitudinal optical field. A collimated linearly polarized laser beam, with along x-axis polarization, was incident from the bottom glass side on the plasmonic lens. The incident light focused by the plasmonic lens interacted with the silver-coated tip apex and enhanced the Raman signal of the sample locally. The scattered Raman signal was gathered by a parabolic mirror and detected with a Raman spectroscopy. Then, the plasmonic lens based setup was employed to investigate carbon nanotubes and TERS experiment was performed. Experimental results indicate that the Raman signal is considerably enhanced which proves that the novel TERS configuration is feasible and promising.

Keywords : longitudinal electric field, plasmonics, raman spectroscopy, tip-enhancement