

Nanoscale characterization of graphene and polymer blends using tip-enhanced Raman spectroscopy and 3D surface-enhanced Raman spectroscopy

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This thesis involves the nanoscale characterizations of nanomaterial using novel Raman spectroscopic methods. Raman spectroscopy is an established technique for the characterization of graphene and polymers. However, its spatial resolution is limited by the diffraction limit of light (generally no better than 300 nm), and also affected by refraction when the probing spot is deep within polymer (could be worse than 20 μm in Z axis). This study overcomes these limits by using tip-enhanced Raman spectroscopy (TERS) and three dimensional surface enhanced Raman spectroscopy (3D SERS). Using the near-field enhancement of metallic nanotips, TERS can individually probe each nanostructure on epitaxial graphene. Decreased graphene content in the sub-micron crack, which cannot be resolved by conventional Raman spectroscopy, was observed. For the first time, compressive strain relaxation on graphene nanoridges was measured. This is direct evidence to the 'strain relaxation mechanism' of nanoridges formation on graphene due to mismatch in thermal expansion coefficient. By analyzing nanoridges on graphene microisland, the alternative mechanism of 'Si vapor trapping' also showed to be insufficient to explain the formation. To improve spatial resolution in Z axis within polymer, 3D SERS using highly symmetric nanoporous silver microparticle was developed. Since the plasmon resonance of this substrate originates from uniformly distributed nanopores instead of random aggregation as in aggregated nanoparticle system. The 3D enhancement pattern is highly predictable and resembles particle shape. The octahedrally symmetric shape of the microparticles further provides the predictability. With the substrate, SERS signal from three dimensional volume of target sample can be obtained. Since the particle shape constrains the signal enhancement to the volume near the particle surface, the problem of laser spot expansion in Z axis could be relieved, resulting in improved resolution in the axis.