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iHR320 Imaging Spectrometer and Synapse CCD for SERS substrate analysis

Experimental Assessment of Metal Nanostructures as Effective SERS Substrates

Introduction

Research in nanoscience has garnered much interest because of the different properties of small structures compared to the respective bulk material. The unique properties of nanostructures make them important in biological imaging, diagnostics and therapeutics, drug-delivery, and Surface-Enhanced Raman Spectroscopy (SERS). Metal nanoparticles, specifically Ag and Au, are attractive for medical applications because of their lack of biotoxicity. Study of nanoparticles is interesting because their intrinsic properties can be tuned by varying their size, structure, and composition.[1–3]

SERS enhances Raman scattering and thus increases sensitivity for detection of trace species, even down to single-molecule measurements. Enhancement is attributed to an increase in the local electromagnetic field caused by oscillations of free electrons in the metal substrate, termed Surface Plasmon Resonance (SPR). The degree of enhancement depends on the surface's structure; novel nanostructure synthesis seeks both sensitivity and reproducibility over a wide surface area. In addition to structural considerations, control of the SPR frequency is important in SERS measurements. Precise frequency-control allows matching of a laser wavelength or molecular vibration for Raman measurements, further increasing sensitivity.[1–3]

Experiment

Nanostructures are characterized using a variety of techniques; their performance as Raman-enhancing substrates is assessed with a spectrometer, detector and microscope. Specifically, the excitation laser is
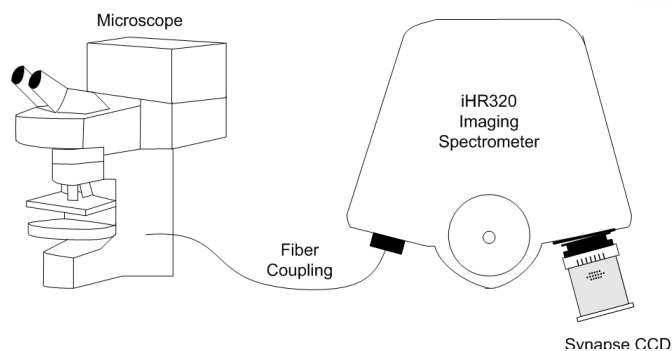

Fig. 1. Typical scattering experiment.

introduced through the microscope objective to the sample (e.g., R6G dye molecules). The back-scattered Raman signal is collected through the objective, coupled into an optical fiber, and directed into a HORIBA iHR320 imaging spectrometer, where the signal is dispersed into its monochromatic components (Fig. 1). A multi-channel Synapse CCD detects the resulting signal as a function of wavenumber-shift from the excitation laser. Experiments are performed with and without the nanostructure substrate to quantify Raman signal-enhancement.[1]

Examples

Many studies with HORIBA instruments have carried out such scattering measurements. One study from the University of Texas at San Antonio (UTSA) synthesized Ag flower-shaped nanostructures. SERS spectra of R6G dye molecules were recorded using 785 nm excitation and a HORIBA iHR320 imaging spectrometer. SEM images and SERS spectra were recorded (Fig. 2, top), with curves for the bare dye molecule (lower) and the enhanced Raman spectrum with an Ag "nanoflower"

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substrate (upper). Spectral peaks correspond to C–C stretching modes, and are enhanced 7–8 orders of magnitude over the bare molecule.[2]

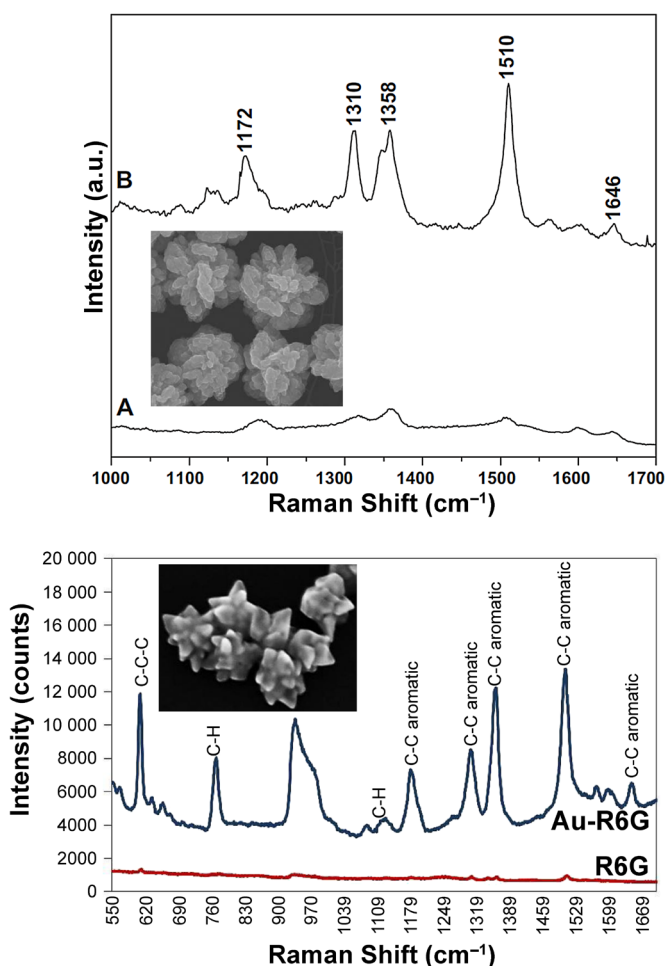Another UTSA study synthesized Au nanostructures with star-like formations. SERS spectra (Fig. 2, bottom) of dye molecules were recorded as above with (upper curve) and without (lower curve) the Au "nanostar" substrate. Labeled spectral assignments correspond to various vibrational modes of the dye molecule. A strong enhancement in the Raman signal is evident with the Au nanostar substrate. Cytotoxicity studies indicated biocompatibility with macrophages, suggesting that Au nanostars would serve as a good substrate for biomedical applications.[3]

A third study from the University of Central Florida controlled the plasmon-resonance frequency. A gold nanoparticle layer was deposited on an Al layer, after which the Al substrate was anodized to an oxide; thickness was controlled by anodization voltage. Scattering spectra were recorded, and indicated a blue-shift in SPR frequency as oxide-layer thickness increased. Thus the SPR frequency can be tuned accurately and reproducibly to optimize SERS.[1]

Conclusions

Metallic nanostructures provide ideal substrates for SERS measurements. Enhancement factors of nearly an order of magnitude are attained using novel Ag and Au nanoparticles. In addition, a technique is described to control the frequency of the SPR to further optimize SERS measurements. HORIBA spectrometers and detectors plus microscopes provide a means for quantifying SERS enhancement factors and surface-plasmon resonance frequencies.

Fig. 2. Raman spectra of R6G dye molecules enhanced by Ag "nanoflowers" (top)[2] and Au "nanostars" (bottom).[3] The upper curves in each panel are SERS-enhanced spectra; lower curves are Raman spectra of the bare R6G.

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