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Ag Nanoparticles As An Efficient Mediator for Patterning, Analysis, and Recognition of 2-D Monolayers

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Noble metallic nanostructures exhibit a phenomenon known as surface-enhanced Raman scattering (SERS) in which the scattering cross sections are dramatically enhanced for molecules adsorbed thereon. Thanks to the enormously large enhancement factor (EF) on the order of 10^6, one can readily acquire the vibrational spectra from adsorbates on roughened metal surfaces, especially noble metals like Au, Ag, and Cu. In recent years, it has been reported that even single molecule spectroscopy is possible by SERS, suggesting that the EF can reach as much as 10^{14}-10^{15} ; at the present, however, it is unclear what mechanisms and structural factors are responsible for single-molecule and single-particle SERS. At least in conventional SERS, it is believed that two enhancement mechanisms, one called a long-range electromagnetic (EM) effect and the other called a short-range chemical (CHEM) effect, are simultaneously operative. The EM mechanism, contributing a factor of 10^4 to the overall EF, is based on the amplified electromagnetic field generated upon optical excitation of surface plasmon resonances of nanoscale surface roughness features in the 10-100 nm range. The CHEM enhancement mechanism, contributing an additional EF = 10^1-10^2, is associated with the electronic coupling of molecules adsorbed on certain surface sites in atomic scale roughness (such as atomic clusters, terraces, and steps) with the surface, leading to a situation similar to resonance Raman scattering. Both mechanisms suggest the possibility of enhanced absorption and enhanced photochemistry for surface-adsorbed molecules. In this symposium, we hope to present our latest observation that patterning of binary monolayers can be accomplished via the Ag nanoparticle-directed photoreaction. We will also illustrate that vibrational spectra of molecules

assembled on SERS-inactive substrates can be obtained by allowing them to be in an indirect contact with laser-ablated Ag nanoparticles. Silver nanoparticles capped with organoisocyanide and host or guest molecules will also be demonstrated to be a very effective molecular sensing/recognition mediator via surface-enhanced Raman spectroscopy.