Improving the molecular specificity of surface-enhanced Raman spectroscopy

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The synthesis of silver colloid particles with controlled size significantly increases the application range of surface-enhanced Raman spectroscopy.

Silver nanoparticles are currently generating significant interest due to their attractive physicochemical properties. In recent years, they have demonstrated their potential in catalysis and electronics applications,\(^1,2\) in the fabrication of highly sensitive detectors,\(^3\) and as substrates for surface-enhanced Raman spectroscopy (SERS).\(^4\)

Since their usage depends on particle characteristics such as size, size distribution, and charge, our present research is focused on the fabrication of SERS-active nanoparticles using synthesis approaches that allow particle size control. Recently, our group used sugars as reducing agents and ammonia as a complexing agent to produce silver nanoparticles ranging in size from tens to hundreds of nanometers (see Figures 1 and 2).\(^5\)

Our interest in producing SERS-active silver nanoparticles is motivated by the wide use of SERS, a powerful chemical sensing technique that combines extremely low detection limits with high molecular specificity.\(^6\) SERS and surface-enhanced resonant Raman spectroscopy (SERRS) are routinely used for investigating the adsorption of simple organic molecules on silver films and colloids. Recent examples include 1,10-phenanthroline,\(^7\) p-nitrothiophenol,\(^8\) 1,4-dihydrazinophthalazine,\(^9\) fatty acids,\(^10\) and nucleic bases and their derivatives.\(^11\) More recently, oxygen release in hemoglobin, the oxygen carrier in blood, was studied with SERRS using silver colloids.\(^12\)

Having overcome earlier signal reproducibility problems associated with the preparation and activation of silver particles, SERS has now emerged as a reliable analytical method. It can now be used as a sensitive probe of ultra-low DNA concentrations adsorbed on colloidal silver\(^11\), of capillary electrophoresis...
eluent\textsuperscript{13}, and also for the quantitative determination of picomolar amounts of important industrial and biological compounds.

The high level of signal enhancement in SERS and SERRS also enables the detection of individual molecules adsorbed on silver particles. Several studies have shown that Raman enhancement factors of the order of $10^{14}$ to $10^{15}$ can be gained using particles of an appropriate size, which depends on the selected laser excitation wavelength. For example, particles in the 70 to 200nm size range require excitation in the 488 to 647nm interval. This is in good agreement with results showing that 80 to 100nm-sized particles (≈50nm in diameter). In this case, however, it is necessary to activate the silver particles, which results in a partial aggregation process producing slightly enlarged particles.\textsuperscript{15} Halide ions (excluding fluorites) are the most commonly used activation agent.\textsuperscript{16}

Our research suggests that the synthesis of size-controlled silver colloid nanoparticles has great potential for the development of novel SERS applications in chemistry and biology.

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