The advancement of nanoscience and nanotechnology has contributed to the development of relevant applications. Noble metal nanoparticles (for example, Au and Ag), present a surface plasmon resonance (SPR) which allows their applications in optical devises, solar cells, photonics, biosensors and surface enhanced Raman spectroscopy (SERS). Recently, silver and gold polyhedral nanostructures have generated interest in its use as SERS substrates due to the high detection sensitivity of molecules such as neurotransmitters, pesticides, cancer biomarkers and others. The increase in sensitivity of the Raman signal is strongly influenced by the particle density and the morphology and arrangement of the nanostructures that conform the substrate. The SERS substrates with the largest reported enhancement factor (EF) are obtained by expensive techniques such as electron beam lithography and physical vapor deposition. On the other hand, the electrochemical methods offer a high control of shape and size, and it represents a low cost alternative process for the fabrication of SERS substrates. In the present work, polyhedral structures of Ag@Au were grown by electrodeposition on indium tin oxide (ITO) substrates, using 1.0 to 10 V during relatively short times (between 1 and 180 s). The polyhedral structures of Ag@Au-coated ITO substrates were characterized by Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD) and Ultraviolet-Visible Spectroscopy (UV-Vis). Using these substrates well-resolved spectra can be obtained Rodhamine 6G (R6G) solutions with concentrations as low as $10^{-6}$ and $10^{-9}$ M. The analytical EF calculated of the SERS substrates were about $10^3$-$10^4$, which are enough to detect analytes at concentrations below 1 ppm. This study provides a simple, fast, reproducible and low-cost process for the fabrication of SERS substrates with a good control of polyhedral morphology without the use of surfactant agents, seeds or templates.

**Keywords:** Surface-Enhanced Raman Spectroscopy (SERS), Ag@Au polyhedral structures, Electrodeposition

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