Surface-enhanced Raman spectroscopy with monolithic, hierarchical nanoporous gold disk substrates

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Surface-enhanced Raman spectroscopy (SERS) has been widely used for highsensitivity molecular detection and identification. When a molecule of interest is near the nanostructured surface of a noble metal such as gold or silver, the localized surface plasmon resonance (LSPR) effect can boost the Raman scattering by many orders of magnitude. Because LSPR is a near-field phenomenon and decays rapidly with increased separation distance between the molecule and the nanostructure, SERS signal primarily arises from the molecules residing within a few nanometers of the nanostructured surface. Therefore, it is advantageous for a SERS substrate to have a large surface-to-volume ratio from the standpoint of high-density "hot spots", as well as optical collection efficiency.

In this paper, we present various forms of monolithic nanoporous gold substrates for effective SERS measurement over large area (Fig. 1). Specifically, we study NPG nanofilms with various porosity by controlled dealloying, and its applications in molecular sensing. We also study patterned NPG structures, which represent a novel hierarchical nanostructure with unit size ~500 nm and pore size ~7 nm (Fig. 2). We show that orders of magnitude larger SERS enhancement factor can be obtained by the additional nano patterning process (Fig. 3) [1]. A plausible explanation will be discussed. NPG-based plasmonic materials are potentially advantageous molecular sensing substrates compared to solution aggregated nanoparticles which suffer from large variability and poor long-term stability. In addition, NPG-based materials could provide a new platform for studying surface chemistry and engineering.

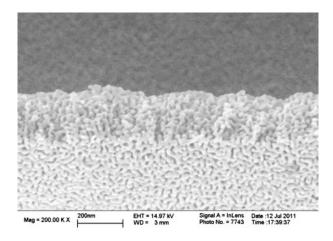


Fig. 1. Nanoporous gold films after nitric acid dealloying.

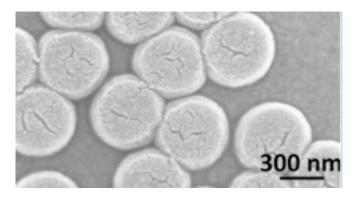


Fig. 2. Nanoporous gold disks.

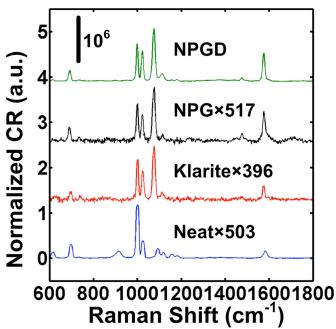


Fig. 3. Normalized count rate (CR) from NPG nanodisks, unpatterned NPG nanofilms, commercial SERS substrate (Klarite, Renishaw), and neat benzenethiol vs. Raman shift (cm⁻¹).

Reference:

[1] J. Qi, P. Motwani, M. Gheewala, C. Brennan, JC Wolfe and W.-C. Shih, "Surface-enhanced Raman spectroscopy with monolithic nanoporous gold disk substrates," Nanoscale, DOI: 10.1039/C2NR33242F.