Improving the performance of SERS substrates by controlling the nano-silver dendrite formation process

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Abstract

Ag nanodendrites fabricated by displacement reactions of base metal nanoparticles have been utilized as SERS substrates. By comparing our substrate with some commercial products, we found that it was superior for detection of volatile molecules such as methyl mercaptan (MM) and naphthalene thiol, and further investigated its suitability for detection of other alkanethiols and different volatile molecules. In addition, the structure of the Ag nanodendrites can be precisely controlled by adjusting fabrication parameters (particle size, deposition thickness, reaction temperature, etc.) in the fabrication process consisting of (1) formation of a high-density monolayer of silica nanoparticles on a glass slide, (2) vacuum deposition of base metals such as copper, and (3) further immersion in silver nitrate solution. By optimizing these conditions, it is possible to further improve the performance of SERS substrates. On the other hand, one of the unsolved problems is that the growth of Ag nanodentrites is not uniform.

Experimental method

Silica nanoparticles are adsorbed within a circular spot (3 mm diameter) region on a glass slide, and copper is vacuum deposited to form a cap-like Cu nanoparticle structure (60 nm thick). Immediately afterwards, they are immersed in 0.1 M $AgNO_3$ solution, subjected to a displacement reaction for 15 min at room temperature, and air-dried to form nano-silver tree-type SERS substrates. The substrates are then exposed to naphthalenethiol, propanethiol, and butanethiol for 15 min, and SERS spectra are acquired using micro-Raman (Nicolet Almega XR, Thermo Fisher Scientific). (Excitation wavelength: 633 nm, irradiation intensity: 67 μW, exposure time: 1 s, number of integration: 16 times) As an additional experiment to gain insight into homogenization, we attempted to acquire SERS spectra during the growth of the Ag nanodendrite. A Raman probe was added to the 0.1 M $AgNO_3$ solution used for the displacement reaction, and the SERS spectrum of the probe was acquired as soon as the displacement reaction started.

Results and Discussion

The SERS spectra of naphthalenethiol, propanethiol, and butanethiol were easily obtained. The sensitivity was found to be significantly above average while they were not necessarily detectable in comparative experiments using commercially available substrates.

For the acquisition of SERS spectra of Raman probes during the growth of Ag nanodendrites, the probe need to be carefully selected, and molecules that are soluble in silver nitrate solution and have SERS activity are investigated. We consider dimethyl sulfoxide (DMSO) to be a good candidate because it is soluble in silver nitrate solution and SERS spectra can be obtained from nano-silver substrates. In addition to the Raman probe to be used, we are still investigating the recovery of copper nanoparticles and the displacement reaction in an inert atmosphere, and we hope that the results will be of great help in finding the optimal conditions for fabrication of Ag nanodendrites.