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Chemically-synthesized highly-symmetric nanoporous silver microparticles for 3D surface-enhanced Raman spectroscopy

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[Introduction] Recently, many developments of 3D SERS substrates have been made because they provide feasible aspects such as large surface area and large numbers of hotspots. These two properties produce very strong SERS signal and versatility in structural adjustment. Since SERS imaging is a technique which yields detailed SERS information in spatial dimension, it is an ideal tool for the characterization and application of 3D SERS substrate. However, 2D SERS imaging does not fully utilize the three dimensionality of 3D substrate. In this study, a suitable 3D SERS substrate for 3D SERS imaging was synthesized, and 3D imaging was used to explore the SERS properties the nanoporous, highly symmetric SERS substrate.

[Experiment] AgCl microparticles are prepared from controlled precipitation reaction between $AgNO_3$ and NaCl by using NH3 as a regulating agent. The various concentrations of the three species can be used to govern the shape of the resulting AgCl particles into hexapod, octapod, octahedron, and caged octahedron. The hexapod AgCl particles were then converted into nanoporous silver microparticles by in-place galvanic reduction using Zinc plate in NaCl solution. The resulting Ag particles retained the hexapod shape, but acquired nanoporousity, which enables SERS effect. Elemental analysis with energy-dispersive X-ray spectroscopy (EDX) confirmed that the particles are 99.99% silver.[1] 3D SERS imaging was done using 514 nm laser and PATP as the probe molecule.

[Result and Discussion] The nanoporous silver microparticles exhibits high SERS enhancement. PATP down to 10^{-8} M concentration can be easily detected.[2] SERS enhancement pattern in 3D closely resembles the 3D hexapod geometry of the particles, which is very regular and very symmetric.[3] This allows the enhancement pattern to be very predictable. Since the enhancement is regular, when the particles are embedded in a real-life sample and the irregularity in signal from 3D imaging is detect, this is certainly come from the inhomogeneity of the sample.

The capability of 3D SERS using the silver nanoporous particles in the detection of the inhomogeneity in polymer blend and double layer polymeric system, have been demonstrated in this study. Compared to the normal 3D Raman, which has worsened Z-axis spatial resolution due to the refraction at the polymer interface, the signal in each point of 3D SERS is confined to the volume near the surface of the polymer. Therefore, the signal from specific small region or layer can be acquired with much less averaging in Z axis. Thus, the inhomogeneity can be easily detected.

[Conclusion] Highly-symmetric nanoporous silver microparticles have been synthesized by purely chemical method. The particles provide highly regular 3D SERS enhancement pattern. This regular pattern allows the detection of the inhomogeneity in polymer blend and double layer polymer.

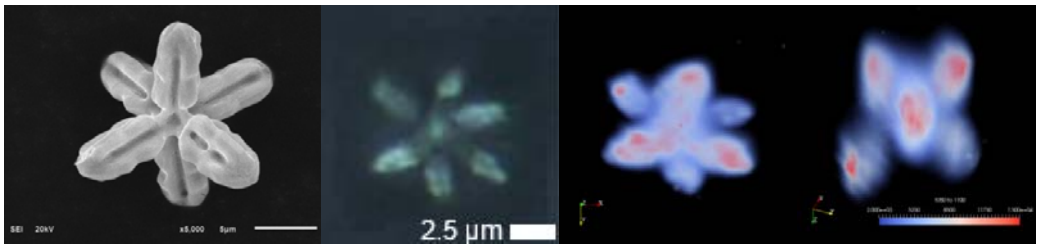

Fig 1. SEM image, optical image, top- and side- view 3D SERS image (using 1074 cm^{-1} PATP band area) of symmetric nanoporous silver particles

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(3) Vantasin, S.; Ji, W.; Tanaka, Y.; Kitahama, Y.; Wang, M.; Wongravee, K.; Gatemala, H.; Ekgasit, S.; Ozaki, Y. 3D SERS Imaging Using Chemically Synthesized Highly Symmetric Nanoporous Silver Microparticles. *Angew. Chem. Int. Ed.* **2016**, *55* (29), 8391–8395.