

Ultrahigh-Density Hot Spots of Surface-Enhanced Raman Scattering

This report features the work of Ying-Huang Lai and his co-workers published in *Adv. Func. Mater.* **24**, 2544 (2014).

According to recent work at Tunghai University in Taichung, hexagonal arrays of nanometer-spaced gold nanoparticles (NP) within a mesostructured polyoxo-methalate (POM)-silicatropic template (Au NP@PSS with POM sites) are suggested to be active three-dimensional (3D) substrates for surface-enhanced Raman scattering (SERS).¹ In *Advanced Functional Materials*, Ying-Huang Lai and co-workers reported that the size, narrow distribution of size and inter-particle distance of Au NP can be finely tailored within the PSS template as anion-exchange cycles enable the PSS to uptake gold ions continuously from the solution subphase for diffusion-controlled and POM-site-directed photochemical reduction inside the silica channels.¹ As revealed by X-ray diffraction, small-angle X-ray scattering and grazing-incidence small-angle X-ray scattering (SAXS) measured at BL23A at the TLS in the NSRRC, the Au NP directed by the PSS template were arrayed into a hexagonal lattice with a mean inter-channel spacing 3.2 nm and had a mean inter-particle spacing 2.8 nm along the channels (see Fig. 1).

Raman spectroscopy provide an important analytical tool to probe the chemical components and elements of materials. In particular, the discovery of SERS greatly enables sensitive detection of single molecules, making it possible to fingerprint molecules in tiny concentrations.² Two commonly accepted mechanisms of enhancement of SERS are an electromagnetic mechanism (EM) and a chemical mechanism (CM). EM that involves enhanced field intensity as a result of the excitation of surface plasmons results in a significantly increased cross section of Raman scattering. In general, EM occurs for molecules absorbed on metal colloids or a roughened metal surface; the enhancement of the EM

is roughly proportional to $|E|^4$ (10^6 - 10^8)— E denotes the intensity of the electromagnetic field. Arrays of metal nanoparticles, as an example, are among the most studied subjects for the EM of SERS.² Relative to EM, CM is an enhancement due to increased polarizability as charges transfer between a molecule and a substrate. The CM contribution to the non-resonant SERS enhancement is small (10 - 10^2). Graphene, as an example, has been intensively studied for large CM enhancement in SERS.³

In principle, these two mechanisms occur concurrently for molecules absorbed on the surface of metal NP, but the EM invariably dominates the enhancement of the Raman signals. In particular, when the gaps between metal particles, which are also known as hot spots, are less than 1 nm, the electromagnetic fields at the gaps become large. As a result, the Raman signals of the molecules located at the gap areas are greatly enhanced by hot spots. To date, numerous designs of two-dimensional (2D) SERS substrates such as arrays of metallic nanostructured objects or surfaces have been suggested, but simple 2D SERS substrates have limited sensitivity because of a limited number density of hot spots (typically less than 10^5 cm⁻³). To increase the sensitivity, 3D porous structures with large surface areas allowing the formation of hot spots are a good candidate.^{1,4} The narrowly spaced Au NP at PSS have an enormous number density (10^{19} NP cm⁻³) and can also provide densely packed hot spots for SERS.¹ These substrates allow the detection of 4-mercaptobenzoic acid (4-MBA) at a molecular level, down to 5 ng. Such a sensitive detection of 4-MBA molecules utilizing efficient 3D SERS substrates opens a path for affordable detection of chemical compounds in trace proportions.

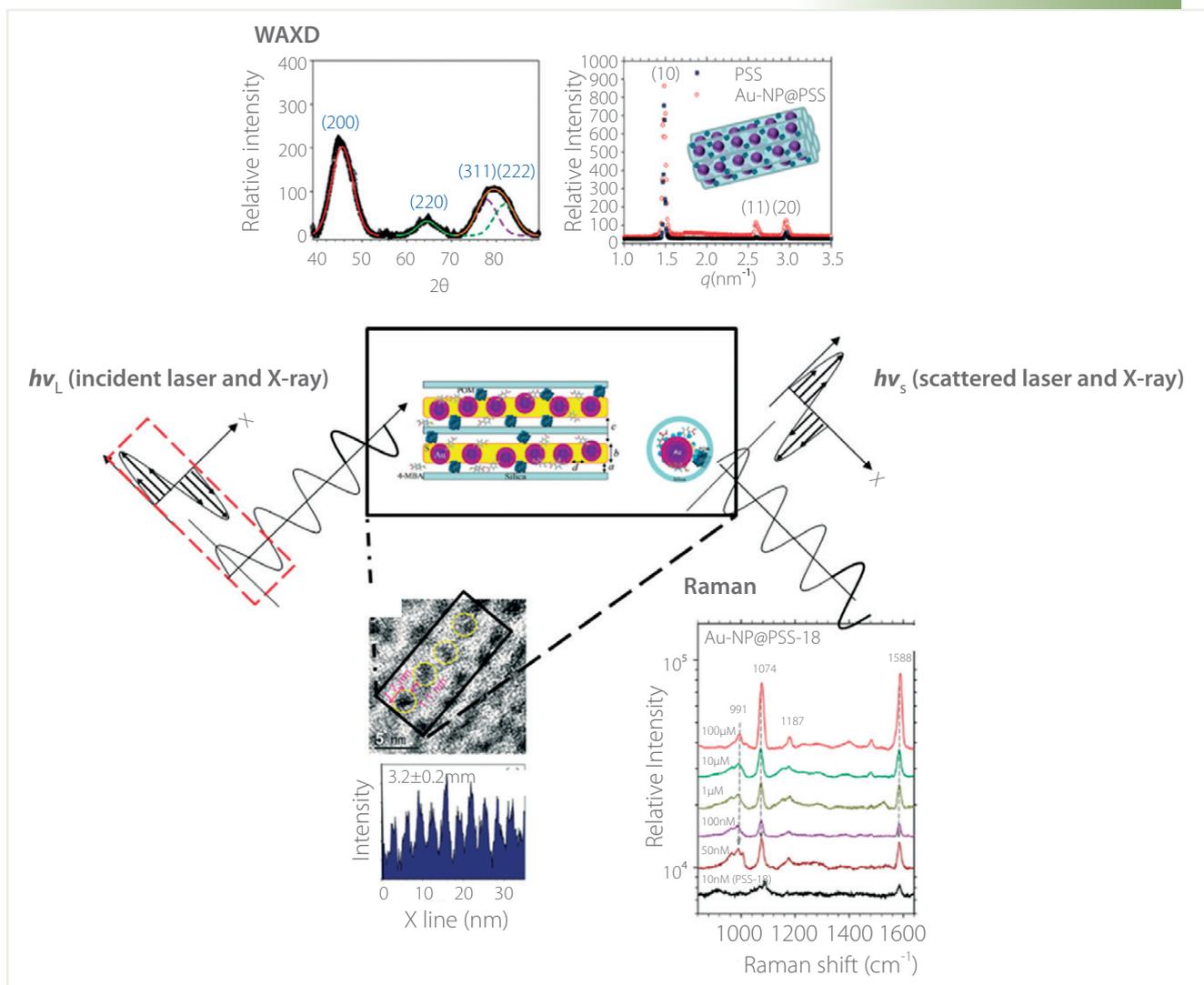


Fig. 1: Schematic of surface-enhanced Raman scattering of 4-MBA absorbed on Au-NP@PSS substrates. The mesostructures of PSS and crystals of Au NP were characterized with SAXS and WAXD. (Adapted from Ref. 1)

References

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