TRIGONAL SILVER NANOSTRUCTURE FOR SINGLE MOLECULE DETECTION WITH SURFACE ENHANCED RAMAN SCATTERING

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Abstract: This presentation gives the fabrication and SERS activity of trigonal silver nanostructures using nanosphere lithography to provide single molecules sensitivity.

One of the dominant factors for the single molecule detection by SERS is nanoscale morphology of the active metal surfaces. Silver or gold nanoparticles prepared by chemical reduction of AgNO₃ or HAuCl₄ have been exploited in most cases³-⁸. This is probably due to experimental feasibility to explore the optimum metal nanoparticles with particular morphology or sizes. However, it has not been established to fabricate such optimum nanoparticles with sufficiently high yield by the chemical reduction, since the process can only be macroscopically controlled with temperature or mixing speed. Indeed, variety of silver particles with different shapes and sizes are formed by means of citrate salt as a reducing chemical, while NaBH₄ provide homogeneous, isolated spherical silver particles with modest enhancement. Obviously, only scarce metal nanoparticles show the blinking among huge number of particles, e.g. < 1 % of the entire particles³-⁸. Chemically etched metal surfaces could provide much higher occurrence for the blinking in SERS as suggested by Nie et al.³ However, SERS spectrum is strongly dependent on the nanoscale morphology at the active sites which is not precisely controlled with the etching conditions.

Based on the theoretical simulation, trigonal silver nanoprism was fabricated by means of nanosphere lithography that has been established by Van Duyne’s group¹,². The nanostructure is composed from a two-dimensional (2D) array of trigonal prisms that provides large electric field at their sharp edges under localized surface plasmon resonance⁴,⁷. In fact, it yielded the blinking of SERS signal from adsorbed rhodamine 6G, which is abrupt and repeated intensity fluctuation with time and has been attributed to a single molecule phenomenon. The blinking occurred on the trigonal metal nanostructure approximately 20 times as efficient as that on continuous silver films, prepared with the same evaporation condition as for the trigonal structure. Furthermore, the blinking was not observed on the continuous silver films after annealed at 473 K for 2 h, of which active sites (junctions) had been extinguished by coalescence of granular silver particles as evidenced by AFM images⁹. It has been proved experimentally that the blinking in SERS was observed quite efficiently on the silver surface with sharp edges as well as junctions⁶-⁸. Consequently, the trigonal silver nanostructure fabricated here is quite efficient to give single molecule sensitivity in SERS.

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References:

Fig. 1 AFM image of the trigonal Ag nanostructures prepared by nanosphere lithography.

**Blinking frequencies on trigonal Ag nanostructure and continuous Ag films**

Fig. 2 Blinking probability at the trigonal Ag nanostructures and continuous film region. Sampled area consists of 108 unit area with 7×7 spots, where each spot is composed from 4 × 4 pixels of CCD with a size of 1µm × 1µm at the sample position. Numbers of blinking spot in each area were counted for 10 sec. As a summary, 1) dark region (spot = 0): 9.6 % for trigonal, 37% for continuous, 2) > 5 spots region: 61 % for trigonal, 26 % for continuous, in other words ca. 30 times more efficient based on occupied area by trigonal structures, and 3) blinking is completely suppressed by annealing of continuous film. The trigonal Ag nanostructure is quite efficient to observe the blinking for SMS-SERS.