SINGLE MOLECULE DETECTION OF 4-DIMETHYLAMINOAZOBENZENE BY SERS

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Abstract: Single molecule SERS spectra of 4-dimethylaminoazobenzene (DAB) adsorbed on the silver colloid were observed in this paper. Spectral diffusion of Raman shift with time from the molecule adsorbed on the silver surface is reported by the first time according to our knowledge.

Single Molecule Detection is of great scientific and practical significance in many fields such as chemistry, biology, medicine, pharmacology, and environment science [1]. Traditional statistical measurement shows the average properties of a great number of molecules, while single molecule detection can provide the information of a single molecule in unbalance system on the structure and function of single molecule. Surface-enhanced Raman scattering (SERS) is widely used as a highly sensitive analytical tool for molecular detection. Some studies showed that single molecule could be probed by SERS [2, 3]. DAB is an important azo dye, which is widely applied to the production of wax products and polystyrene products. Also DAB is considered a human carcinogen based on the study of experimental animals. Many studies were focused on the structure of DAB molecule before, while there were very few works on trace detection. In this paper, the SERS spectra of single molecule DAB are reported based on the observation of blinking of SERS signal and spectra diffusion of Raman shift with time.

Colloidal silver nanoparticles were prepared in an aqueous solution by the reduction of silver nitrate with sodium citrate following the method reported by Lee and Meisel [4]. The samples were prepared by incubating 1ml of the NaCl activated silver sol with 1μl of the solution of DAB/$CHCl_3$ at the concentration of 10^{-7} M, resulting in the final sample concentration of 1×10^{-10} M. A droplet of a few μl prepared sample was dropped on cleaning aluminum foil to measure. SERS spectra were recorded by using Renishaw RM-1000 Raman microscopic spectrometer with a 632.8nm excitation. The SERS spectra were measured for 100 times continuously with accumulation of 1 second through 20X microscope lens. The original silver sol prepared had an UV-VIS absorption peak at 420nm and the average diameter of the silver particles was about 50 nm from the TEM measurement. After adding the NaCl and DAB, another wide absorption band in 600-800 nm range appeared, which indicated the aggregation of silver nanoparticles. The probed volume from the laser excitation in our sample was estimated to be approximately a cylinder [5] of diameter about 2×10^{-4} cm and length about 10×10^{-4} cm, which was to be about 3.1×10^{-14} liter. The final sample concentration of DAB was 1×10^{-10} M, which means an average of 1.8 molecules in the probed volume. Brownian motion of single-DAB-molecule-loaded silver particle into and out of the probed volume results in large statistical changes in SERS signals measured from such a sample in time sequence, which is called blinking. The average residence time of a silver particle in the scattering volume is estimated about 1s based on Brownian diffusion in water [5] that becomes comparable with our measurement time. Fig.1 shows one group of 100 SERS spectra of DAB spectral diffusion of Raman shift with time from the molecule adsorbed on the silver was observed. For instance, the Raman band representing

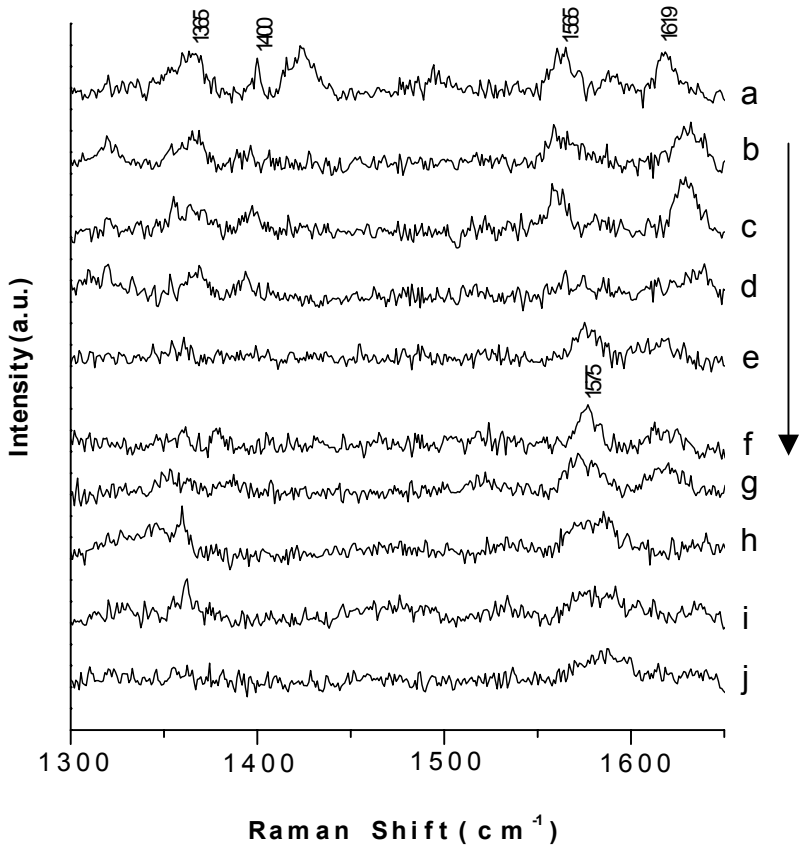

Fig.1 Time-resolved SERS spectra of DAB molecule adsorbed on silver particle. The a average number of DAB molecule in the probed volume was 1.8. The spectra were measured continuously with accumulation time of 1 second. The arrow shows time sequence.

C-C stretch and C-C in-plane bend modes appears at 1590 cm^{-1} in ensemble measurement, while it appears at about 1565 cm^{-1} in spectrum a, b, and c; 1575 cm^{-1} in spectrum d, e, f, g, and h; 1590 cm^{-1} in spectrum i and j. These could be due to the difference of interaction between varied single molecule and varied silver particle, for instance, due to the different adsorption states of DAB molecule on the silver surface. A Poisson distribution of the Raman signal from the SERS spectra was also observed.

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