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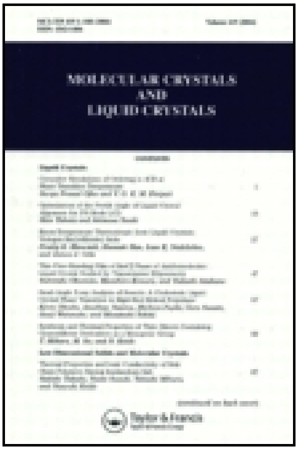

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Gold Nanoparticles Assembly as the Model System in Studying Mechanisms of Surface Enhanced Raman Scattering

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Gold Nanoparticles Assembly as the Model System in Studying Mechanisms of Surface Enhanced Raman Scattering

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Colloidal gold nanoparticles were immobilized on to a solid surface through a bifunctional self-assembled monolayer, forming a sandwiched structure in the form of [gold nanoparticulate film]/[self-assembled monolayer]/[solid surface]. Thus prepared model system was used to study the mechanisms of surface enhanced Raman scattering(SERS). A preliminary result is given in this paper on particle size and potential dependencies of surface enhancement of Raman scattering.

Keywords: Gold nanoparticles; Self-assembled monolayer; SERS

INTRODUCTION

Currently, there are two popularly accepted origins of Raman enhancement, *i.e.*, electromagnetic and chemical enhancements[1]. The former comes from the local field enhancement caused by the rough metal surface, and the latter is attributed to the charge transfer between the adsorbed molecules and the metal substrates. Deep understanding of the enhancement mechanisms greatly depends on the quantitative correlation between the Raman enhancement and the structural features of the SERS-active systems. The key point is to get a SERS-active substrate with well-characterized surface structures, it is one of the frontiers in the field of SERS[2].

Although electrochemically roughened gold electrodes and colloidal gold suspensions have long been used as SERS-active substrates, they are not ideal as the model system in the structural correlation studies, due to the inability in controlling and determining their exact structural parameters. We have noted the recent works by Natan's group[3] and Cotton' group[4], in which they claimed that by immobilizing monodispersed colloidal gold nanoparticles onto solid surface, nearly perfect SERS-active substrates with uniform roughness only defined by the particle size and distribution, can be obtained. We have extended this idea to the preparation of SERS-active substrates by assembling gold colloids onto conductive surface (e.g. gold) using self-assembled monolayer (SAM) as the coupling layer, and addressed the possibility for thus prepared nanoparticles assembly being used as the model system in studying the mechanism of Raman enhancements[5].

In the present work, a self-assembled monolayer of p-aminothiophenol(p-ATP), a molecule with large Raman cross-section, was adopted as the coupling layer and served as the Raman probe to characterize the SERS-activity of the nanoparticles assembly. With this configuration, we can readily change the surface roughness in a controlled manner by changing the size of the nanoparticles. The conductive gold substrate also makes it possible to study the chemical effect by potential-dependent measurements.

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EXPERIMENTAL

p-Aminothiophenol(p-ATP) was from Aldrich(USA) and used as received. Ultrapure water (>17MΩ·cm) was used throughout the experiments. Method for preparing the nanoparticles assembly is similar to that previously described[5,6]. The average size of the synthesized colloidal gold nanoparticles was determined by transmission electron microscopy. Raman spectra were taken with a Renishaw System 1000 Ramascope excited at 632.8nm(He-Ne laser).

RESULTS AND DISCUSSION

Size-dependence of Raman enhancement

Substrate morphology dependence of Raman enhancement is one of the most important data to deduce mechanisms of Raman enhancement. Some theoretical and experimental studies on silver substrates have been reported[7], and the optimum feature size for the maximum enhancement was determined ranging from 80 to 100nm. However, little has been known for gold substrates, except the theoretical calculations by Schatz et al., who used spherical gold particles as the model and gave an particle size of 60nm for the maximum enhancement[8].

We experimentally studied the size dependence of SERS intensity, by assembling gold nanoparticles of different sizes, 12nm, 25nm, 40nm and 70nm. The result is given in Fig. 1, spectra shown in the left were obtained from p-ATP SAMs covered by gold nanoparticles, and the plot shown in

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the right is the normalized SERS intensity of the band at 1080cm^{-1} (ν_7 mode of the benzene ring in p-ATP) vs. particle size. It can be seen that in the size range explored, the SERS intensity increased with the increase in particle size. However, at the present stage, the optimum size for Raman enhancement has not been determined, because the assembling of nanoparticles larger than 70nm is not as effective as smaller particles. Nevertheless, the ascending trend of the plot at the point of 70nm suggests that the particle size for the maximum enhancement might be slightly larger than the theoretical result(60nm) by Schatz et al.[8]. On the other hand, our result agrees well with the very recent experimental work by Brolo et al.[9], who observed the strongest SERS signal at an averaged size of roughness features of *ca.* 100nm on an ORC-treated gold electrode. Obviously, much work should be done to understand the mismatch between the theoretical and experimental results.

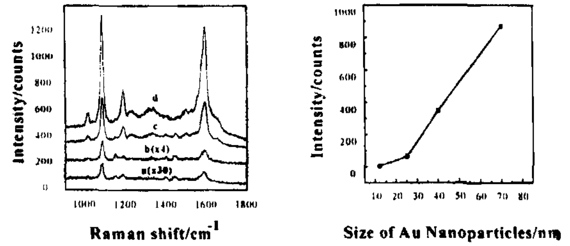

FIGURE 1 Size-dependent SERS spectra(*left*, particle size, a: 12nm, b: 25nm, c: 40nm, d: 70nm), and plot of SERS intensity vs.particle size(*right*)

Potential-dependence of Raman enhancement

We also studied the potential dependence of SERS intensity to probe the chemical contribution to the total enhancement. Fig. 2 shows the potential-dependent SERS spectra of p-ATP from gold nanoparticles (average size 40nm) assembly in 0.1mol·dm^{-3} $NaClO_4$ aqueous solution. The normalized intensities of three bands at 1080 cm^{-1}, 1144 cm^{-1} and 1431 cm^{-1}, are given in Fig. 3, showing that the normalized intensity of different band changes in different way with the applied potential. For example, the bands at 1144 and 1431 cm^{-1} change drastically with the applied potentials, while the band at 1080 cm^{-1} does not show an obvious change. Furthermore, for the former two bands, the intensity-potential curve is asymmetric with a more rapid change at the negative side, giving a maximum at ca. -0.30V. These characters are similar to those for p-ATP on silver surfaces reported in the literature[9], indicating that the charge transfer effect exists in the present system.

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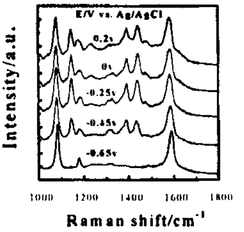

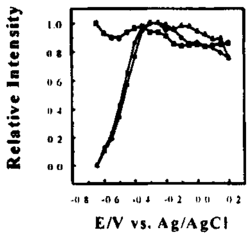

FIGURE 2(*left*) **Potential dependence of the SERS spectra of p-ATP from gold nanoparticles assembly in 0.1 M NaClO$_4$.**

FIGURE 3(*right*) Normalized intensities of the 1080 cm^{-1}(■), 1144 cm^{-1}(●) and 1431 cm^{-1}(Δ) bands, as function of applied potentials.

To further determine the direction of the charge transfer, the usual way is to get the excitation profile of the SERS intensity, that is, to systematically change the excitation wavelength. Since it is difficult to do this experiment with our present Raman system, we tried alternatively to get useful information for deducing the charge transfer direction. In our approach, the size of gold nanoparticles was changed from 40nm to 70nm, similar potential-dependent SERS profiles were obtained, except that the maximum appeared at an applied potential of -0.47V(not shown in Figure). We preliminarily attributed this difference to the different Fermi levels in the nanoparticles of different sizes, and this fact suggests that the charge transfer direction is from gold nanoparticles to p-ATP molecules. Further theoretical and experimental studies are in progress.

Acknowledgments

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References

[1] R.K. Chang and T.E. Furtak(Eds.), *Surface Enhanced Raman Scattering*, Plenum: New York, 1982.

[2] R.P. Van Duyne, J.C. Hulteen, D.A. Treichel, *J. Chem. Phys.*, **99**, 2101(1993).

[3] K.C. Grabar, R.G. Freeman, M. B. Hommer, et al., Anal. *Chem.*, **67**, 35(1995).

[4] G. Chumanov, K. Sokolov, B. Gregory, *et al.*, *J. Phys. Chem.*, **99**, 9466(1995).

[5] T. Zhu, H.Z. Yu, J. Wang, *et al.*, *Chem. Phys. Lett.*, **265**, 334(1996).

[6] T. Zhu, X. Zhang, J. Wang, *et al.*, *Thin Solid Films*, **327–329**, 595(1998).

[7] N. Cross, J.E. Pemberton, *J. Electroanal. Chem.*, **217**, 93(1987).

[8] E.J. Zeman, G.C. Schartz, *J. Phys. Chem.*, **91**, 634(1987).

[9] A.G. Brolo, D.E. Irish, G. Szymanski, J. Lipkowski, *Langmuir*, **14**, 517(1998).

[10] M. Osawa, N. Matsuda, K. Yoshi, *et al.*, *J. Phys. Chem.*, **98**, 12702(1994).