Journal of the Korean Chemical Society
Vol. 36, No. 1, 1992
Printed in the Republic of Korea

구리막대로 응결시킨 은 졸의 라만 스펙트럼

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(1991. 7. 29 접수)

Raman Spectrum of Silver Sol Aggregated by A Cu Rod

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(Received July 29, 1991)

요 약. 구리나 아연 막대에 의하여 은 졸의 응결이 일어난다. 은 졸의 표면에 있는 은 이온이 구리 혹은 아연 금속과의 산화-환원 반응에 의하여 은 금속으로 환원되면서 응결이 일어난다고 여겨진다. 구리 막대로 응결시킨 은 졸의 라만 스펙트럼을 연구하였다. 은 콜로이드 표면에 붕산과 질산 이온이 흡착되어 있다는 증거를 발견하였다. 은 콜로이드 표면에 흡착된 이들 이온들은 첨가된 흡착제에 의하여 쉽게 치환된다는 사실 또한 발견하였다.

ABSTRACT. Silver sols are aggregated by a Cu or Zn rod. This is maybe due to the reduction of Ag^+ ion on the surfaces of silver sols to Ag metal by oxidation-reduction reaction with Cu or Zn metal. Raman spectra of silver sols aggregated by a Cu rod have been studied. The evidence of borate and nitrate ions adsorbed on silver colloid surfaces is found. It is also found that these ions adsorbed on silver colloid surfaces are easily replaced by adsorbated added.

INTRODUCTION

Surface-enhanced Raman Scattering (SERS) spectroscopy[1] is a well-established method for studying properties of molecules adsorbed on specially prepared metal surfaces like silver, gold, and copper.

The colour of an aqueous silver sol is changed from yellow to blue when adsorbate such as pyridine is added. This color change is known to be due to aggregation of colloid particles[2]. The aggregation mechanism is thought to involve an adsorption of oppositely charged adsorbates on the colloid particles so that stabilizing surface charge undergoes a progressive neutralization as the concentration of adsorbates is increased. It is also known that the enhancement on the surface of aggregated colloid particles is much greater than that on the surface of an isolated colloid particle[3]. Lots of molecules can not make aggregation of colloid particles when they are added into silver sols. In this case, one can not observe the SERS spectrum due to low enhancement on the surface of an isolated colloid particle. We made aggregation of a silver sol by a Cu or Zn rod, and then added adsorbate into the aggregated sol. In this paper, we report the Raman spectra of silver sols aggregated by a Cu rod.

EXPERIMENTS

Aqueous silver sols were prepared by reducing silver nitrate with sodium borohydride: A sodium borohydride solution (60 m*l* of $2\times10^{-3}M$) was mixed with a silver nitrate solution (22± 2 m*l* of $1\times10^{-3}M$). Silver ions are reduced to silver metal by the borohydride ions. When the two solutions were mixed together, yellow or orange yellow colloid solutions were produced immediately.

Aggregation of silver sols was made by stirring with a Cu or Zn rod in silver sols. The colour of silver sol changed from yellow to red or blue.

A Zn rod was used without any treatment. Several volts of DC was applied to the Cu rod and the Pt electrode which were inserted into a 0.5 *M* KCl solution for 2 minutes. The Cu rod was the anode. The surface of the Cu rod was washed by distilled water before immersing it in silver sols.

15-crown-5 dissolved in water was added into the silver sol aggregated by a Cu rod for Raman study.

Spectra were recorded with a SPEX 1400 series monochromator equipped with photon counting and interfaced to a Tektronix 4052 computer. Sample was excited with a Spectra-Physics Model 165 argon ion laser. Transmission UV-visible spectra were recorded with a Shimadzu Model UV-260 spectrophotometer.

RESULTS AND DISCUSSION

We made aggregation of silver sols by a Cu or Zn rod, without addition of adsorbates. The colour of silver sols was changed from yellow to blue or red.

The absorption spectra of silver sols were shown in *Fig.* 1. Spectrum A is for a pure silver sol whose color was yellow. The absorption maximum is near 390 nm. Spectra B and C are for the silver sols aggregated by a Zn rod, and their colors were red and blue, respectively. We obtained the similar spectra for the silver sols aggregated by a Cu rod, instead of a Zn rod. In spectra B and C, the relative intensity of the band near 390 nm is decreased and a new band is developed near 577 and 626 nm, respectively. The new band developed near 600 nm has been also observed in the absorption spectrum of silver sol when adsorbate such as pyridine was added. By T.E.M. study[2], the development of this new absorption band is due to aggregation of colloid particles. Aggregation does not produce coalescence into larger particles but rather assemblies of apparently randomly adhering spheres each of about the original dimensions. The unaggregated colloid consists of fairly uniform silver spheres approximately 200 Å in diameter.

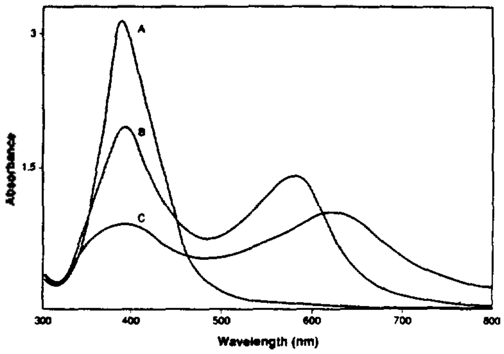

Fig. 1. Transmission UV-visible spectra of a pure silver sol (A), and the silver sols aggregated by a Zn rod (B and C). The colors of the sols for (A), (B) and (C) were yellow, red and blue, respectively.

The aggregation mechanism of silver sols by a Cu or Zn rod can be understood by considering the reduction potential of metal ions. The standard reduction potential of Ag^+, Cu^{2+}, and Zn^{2+} are 0.800, 0.34 and −0.763 volts, respectively. The more positive the reduction potential, the greater the tendency for the substance to accept electrons and become reduced. A large negative reduction potential indicates a strong favoring of the oxidized state. The silver sol made by reducing silver nitrate with sodium borohydride is positively charged due to Ag^+ ions on the surfaces. Therefore, when a Zn or Cu rod is immersed in a silver sol, the oxidation-reduction reaction may take place between silver ion and Zn or Cu metal. Some silver ions on colloid surfaces become silver metal. Consequently, the surface charge is reduced. Therefore, the repulsion force between colloid particles is reduced, and the aggregation of silver colloid particles may take place. The effect of DC applied to a Cu rod is not clear. Anyway, we could not make aggregation of silver sols by a Cu rod which DC was not applied to. The oxide layer of a Cu rod may be removed in the process of applying DC because we have observed the aggregation of silver sols by a Cu rod whose surfaces were rubbed out by a sandpaper. In any case, we could not make aggregation of silver sols by a Pt or Ag rod.

Raman spectra of a pure silver sol (C) and the silver sols aggregated by a Cu rod (A and B) were

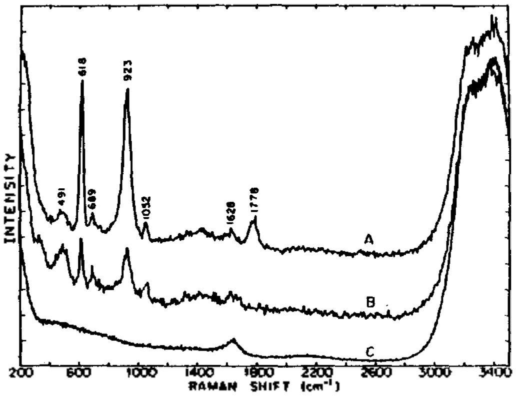

Fig. 2. Raman spectra of silver sols aggregated by a Cu rod (A and B), and a pure silver sol (C). Spectrum B was observed in the most samples and spectrum A was observed in a few samples.

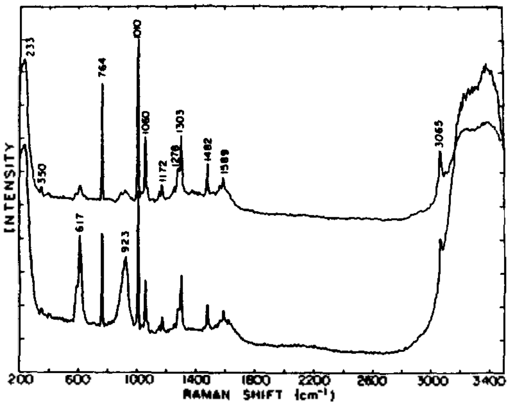

Fig. 3. SERS spectra of 15-crown-5 added in the silver sol aggregated by a Cu rod. The concentration of 15-crown-5 for the upper spectrum is higher than that for the lower one.

shown in *Fig.* 2. In spectrum C, the strong back ground in the low frequency region is due to Rayleigh scattering. The weak broad band near 1600 cm^{-1} and the strong broad band near 3300 cm^{-1} are due to water vibrations. The bands near 1620 and 3300 cm^{-1} in spectra A and B are also due to water vibrations.

Spectrum B was observed in the most silver sols aggregated by a Cu rod, and spectrum A was observed in a few cases. The same Raman spectrum as A has been observed in the several months old silver sol whose color was changed to blue naturally. The bands in spectra A and B are due to the species which exist originally in the silver sol since no adsorbate was added. The strong bands at 618 and 923 cm^{-1} are assigned to borate ion[4,5]. These bands have been observed in the SERS spectra of a few adsorbates which are adsorbed weakly on colloid surfaces[5]. The borate ion is not contained initially in the silver sol but it may be produced from borohydride in the process of reducing of silver ion.

The frequencies of the bands at 689 and 1052 cm^{-1}, and near 1400 cm^{-1} are very close to those of Raman data of KNO_3, 716 (ν_4), 1049 (ν_1), and 1390 (ν_3) cm^{-1}.[4] We assign cautiously these bands to nitrate ion. Nitrate ion is included initially in the sol as silver nitrate. The band at 1778 cm^{-1} is possibly due to borate or nitrate ion. In solid sample, ν_3 a degenerate mode, splits into two bands due to distortion of the molecule[4]. For example, Anbar *et al.*[6] have observed a band at 1755 cm^{-1} in IR spectrum of KNO_3. Generally, by chemical adsorption on surfaces the symmetry of molecules is lowered. Therefore, ν_3 of borate or nitrate ion will split into two bands, and a similar band is expected near 1755 cm^{-1}.

Assignment of the low frequency bands in spectra A and B is not clear. These bands may be due to the deformation of nitrate and borate ions adsorbed on the silver surfaces.

Borate and nitrate ions are on the surface of aggregated colloid particles since only molecules adsorbed on the surface of colloid particles can be observed in the SERS spectrum. There is no doubt that borate and nitrate ions are also adsorbed on the surface of pure silver sol particles. Nevertheless, the bands due to these ions are not observed in the Raman spectrum of a pure silver sol due to the low enhancement on the surfaces of isolated colloid particles (see C in *Fig.* 2). In this case, it should be explained why the bands due to these ions are not observed in the SERS spectra which are strongly enhanced. The reason is found in the Raman spectra of 15-crown-5 added into the silver sol aggregated by a Cu rod (see *Fig.* 3). We could not observe the SERS spectrum of 15-crown-5 added into a pure silver sol.

This means that 15-crown-5 is adsorbed weakly on the surfaces of silver sol particles but the adsorption is not strong enough to make aggregation of colloid particles. In *Fig.* 3, the concentration of 15-crown-5 for the upper spectrum is higher than the lower one. When the concentration of crown ether increased, the intensity of the bands at 617 and 923 cm^{-1} decreased. This is certainly due to the fact that the borate ions on the colloid surfaces are replaced by the 15-crown-5 added. The bands due to nitrate ion are not observed in both spectra of *Fig.* 3. Since borate and nitrate ions adsorbed on the surfaces of silver sol particles are replaced by 15-crown-5 which is a weak adsorbate, they will be replaced completely by strong adsorbated which can make aggregation of colloid particles. Therefore, the bands due to these ions will not be observed in the most SERS spectra.

The SERS spectrum of 15-crown-5 is very different from the Raman spectrum of its liquid or solution. We can find some evidence of chemical reaction in the SERS spectrum. For example, the νCH bands are very strong at 2884 and 2924 cm^{-1} in the liquid spectrum but there is a band at 3065 cm^{-1} in the SERS spectrum (see *Fig.* 3). Furthermore, this frequency corresponds to that of unsaturated carbon-hydrogen stretching. The frequencies of other bands are also similar to those of aromatic ring vibrations.

ACKNOWLEDGEMENT

This paper was supported in part by RESEARCH FUND FOR JUNIOR SCHOLARS, Korea Research Foundation.

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