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ORIGINAL CONTRIBUTION

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Raman scatterings of colloidal silver and gold prepared in the presence of a nonionic surfactant, Surfynol 465

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Abstract The FT-Raman and resonance Raman scatterings of colloidal silver or gold formed in the presence of a nonionic surfactant, Surfynol 465, were studied. The intensity of Raman scattering of colloidal solution was strongly affected by the power of laser for excitation. At the low power, the intensity of scattering and the spectrum of colloidal solution were normal. However, at the high power, the intensity of Raman scattering anomalously increased over the whole frequency region, suggesting the surface enhanced Raman scattering (SERS) on colloidal silver or gold. And in the Raman spectra new bands were found in addition to bands of starting materials. Through the assignment of new bands, the working mechanism of Surfynol 465 for the formation of colloidal silver or gold was discussed.

Key words Surface enhanced Raman scattering – colloidal gold – colloidal silver – nonionic surfactant – Surfynol 465

Introduction

We have studied the solution behavior of a nonionic surfactant, Surfynol 465 [1–3]. Due to the centrally located polar group, Surfynol 465 molecule orients horizontally on the surface to form structured solid films (Fig. 1). For example, the dipping of metal into Surfynol 465 solution makes its surface highly polished [4].

Recently, we found that by simply mixing two aqueous solutions of $HAuCl_4$ and Surfynol 465, colloidal gold formed at room temperature [5, 6]. In the formation of colloidal gold, Surfynol 465 was considered to function as a reducing agent of $HAuCl_4$ and a stabilizing agent of the resultant colloidal gold. Also, we could obtain the colloidal silver from $AgClO_4$ and Surfynol 465 [7]. However, the working mechanism of Surfynol 465 in the formation of colloidal silver or gold could not be examined in detail.

Meanwhile, the surface enhanced Raman scattering (SERS) of pyridine was found through the adsorption on the colloidal silver or gold surface as well as the silver electrode surface [8–10]. In addition to the SERS of pyridine, the SERS of citrate, Cl^-, ethylene, acetylene, ethylene oxide or Triton X has also been reported in the presence of colloidal silver [11–16].

Therefore, it is expected that if any molecule showing Raman scattering in its solution co-exists with the colloidal metal and is adsorbed on the metal surface of colloid, we would observe the SERS in the Raman spectrum of the dispersion system and vice versa [17]. Moreover, the anomalous intensity in the SERS reveals the Raman bands of molecule, whose amount is too small to detect in the ordinary Raman scattering, and we can detect and examine the functional groups which constitute parts of the molecule adsorbed on the colloidal metal and directly interact with the metal surface.

In this work, we found the SERS on colloidal silver or gold formed in the presence of Surfynol 465 to have the

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Raman spectrum with new bands. Through the assignments of Raman bands, the reaction mechanism for the formation of colloidal silver or gold was elucidated.

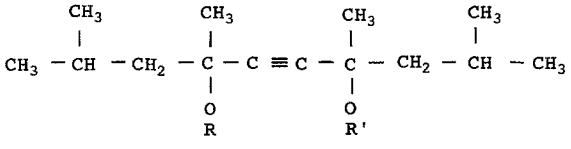
Experimental

Materials

Silver perchlorate hydrate, chloroauric acid trihydrate and polyethylene glycol (PEG, the average molar mass: ca. 400 g mol^{-1}) were obtained from Aldrich Chem. Surfynol 104 and Surfynol 465 were gifts from Air Product and Chemicals, U.S.A. Deuterium oxide was from Merck Co. Ltd. Deionized and distilled water was used.

Preparation of colloidal silver and gold [5–7]

The colloidal silver in H_2O or D_2O was formed by simply mixing equal volumes of two H_2O or D_2O solutions of $AgClO_4$ (0.04 mol kg^{-1}) and Surfynol 465 (0.8 mol kg^{-1}) in a test tube. The colloidal gold in H_2O or D_2O was formed from two H_2O or D_2O solutions of $HAuCl_4$ (0.01 mol kg^{-1}) and Surfynol 465 (1 mol kg^{-1}). For the formation of colloidal silver or gold the irradiation of light was not significant. The UV-VIS spectra of colloidal silver and gold showed the absorption peaks at 405 and 530 nm, respectively (Fig. 2).



Surfynol 104 : R = R' = H

Surfynol 465 : R = - $(CH_2CH_2O-)_mH$

R' = - $(CH_2CH_2O-)_nH$

m+n = 8.5

Fig. 1 Chemical structures of Surfynols

Apparatus

The solution for Raman scattering was sealed in capillary tube (diameter: 1 mm) without the exclusion of air. The FT-Raman scattering of solution was measured by using a Perkin–Elmer 2000R FT-Raman spectrometer with a quartz beam splitter and an InGaAs detector. The excitation was provided with the 1064 nm line of a Nd:YAG laser (Spectron Laser System SL300). The other laser wavelengths were eliminated with an interference filter. The resolution of spectrum was 4 cm^{-1}. The resonance Raman scattering of the solution was measured with a Spex Ramalog-9 Raman spectrometer. The excitation was provided with the 514.5 nm line of an argon ion laser (Spectra-Physics). The resolution of spectrum was 4 cm^{-1}.

Results and discussion

The FT-Raman spectra of starting materials for the preparations of colloidal silver and gold are shown in Fig. 3. The observed Raman frequencies along with their tentative assignments are summarized in Table 1 [18–23]. The Raman band at 2240 cm^{-1} of Surfynol 104 was correlated

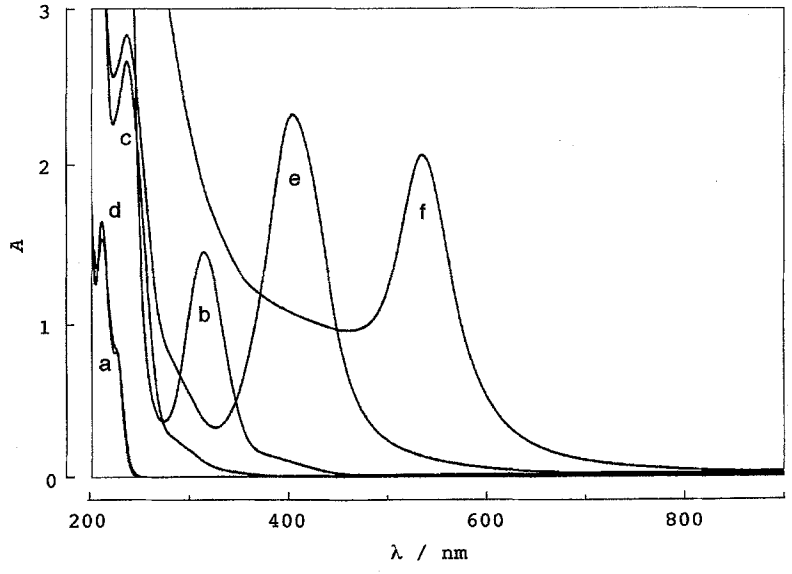


Fig. 2 Ultraviolet-visible spectra of a) $AgClO_4$ aq. (0.02 mol kg^{-1}), b) $HAuCl_4$ aq. (1.5 mmol kg^{-1}), c) Surfynol 465 aq. (0.2 mol kg^{-1}), d) mixture of $AgClO_4$ aq. (0.02 mol kg^{-1}) and PEG aq. (0.5 mol kg^{-1}), e) colloidal silver prepared from $AgClO_4$ aq. (5 mmol kg^{-1}) and Surfynol 465 aq. (0.25 mol kg^{-1}), and f) colloidal gold prepared from $HAuCl_4$ aq. (5 mmol kg^{-1}) and Surfynol 465 aq. (0.5 mol kg^{-1}). The optical path was 1 mm

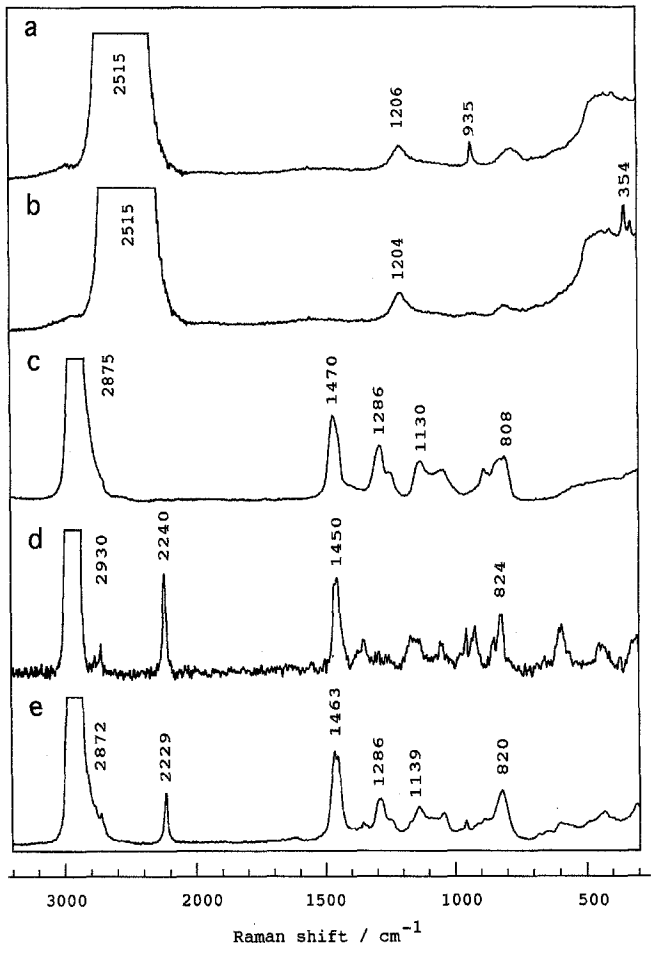


Fig. 3 FT-Raman spectra of a) $AgClO_4$ D_2O solution (0.04 mol kg^{-1}), b) $HAuCl_4$ D_2O solution (0.01 mol kg^{-1}), c) Polyethylene glycol (neat), d) Surfynol 104 (neat), and e) Surfynol 465 (neat). The output power of laser for excitation was 1 W

with the stretching vibration of acetylene [22, 23]. In comparison with the Raman spectra of PEG and Surfynol 104, each band in the spectrum of Surfynol 465 could be assigned.

FT-Raman scattering of colloidal silver

First, the FT-Raman scattering of the mixture of $AgClO_4$ and PEG in H_2O was measured. The FT-Raman spectrum of mixture was the sum of spectra of $AgClO_4$, PEG and H_2O, showing that $AgClO_4$ did not interact with PEG, when the output power of laser provided for excitation was 400 mW. However, when the power was increased to 1 W, a new Raman band appeared at 1769 cm^{-1} (Fig. 4).

Polyethylene glycols undergo autooxidation and degradation in the presence of oxygen gas [24–26]. Through the autooxidation of PEG hydroperoxides with the O–O group are formed, i.e.,

$$-CH_2OCH_2- \text{ or } RCH_2OH + O_2 \leftrightarrow -CH(OOH)OCH_2O- \text{ or } RCH(OOH)OH . \quad (1)$$

The succeeding degradation of hydroperoxides results in the carbonyl compounds with the C=O group. Consequently, hydroperoxides with the O–O group and carbonyl compounds with the C=O group are formed from PEG. The rates of both reactions increase with increasing temperature. At higher temperatures above 60 °C, the rate of degradation is sometimes too large in comparison with that of autooxidation to detect the hydroperoxides.

In the FT-Raman spectrum, the O–O stretching frequency for hydroperoxide and the C=O stretching frequency for aliphatic aldehyde are 900–800 and 1740–1720 cm^{-1}, respectively [22, 23]. Then, the band observed at 1769 cm^{-1} for the mixture of $AgClO_4$ and PEG was estimated to the C=O stretching vibration of carbonyl compounds derived from PEG.

However, when the output power of laser was reduced to 400 mW, we could not observe any band around 1769 cm^{-1}, although the two thermal energies introduced at 400 and 1000 mW became equal in value by changing the irradiation time. Thus, it was supposed that the formation of carbonyl compounds depends mainly on the intensity of laser irradiation. By the irradiation of the PEG aqueous solution with a powerful laser beam, some local temperature in the solution was considered to increase above 60 °C, resulting in the formation of carbonyl compounds through the formation of hydroperoxides.

Meanwhile, it might be considered that atomic silver (Ag(0)) or colloidal silver is formed from silver ion (Ag^+) together with the autooxidation of PEG. However, the UV-VIS spectrum of the mixture of $AgClO_4$ and PEG was the same as that of $AgClO_4$ in H_2O (Fig. 2), showing that colloidal silver could not be formed from $AgClO_4$ and PEG.

Secondly, the Raman scattering of the colloidal silver prepared from $AgClO_4$ and Surfynol 465 in D_2O was studied. When the output power of laser was 100 mW, the FT-Raman spectrum of the colloidal silver in Fig. 5a was at first similar to that of Surfynol 465 (Fig. 3e). After that, the Raman scattering for the same colloidal silver was repeatedly measured in the same condition. The spectra did not change. However, after the colloidal silver was additionally irradiated with a laser of 200 mW for 2 min, new bands were observed in the spectrum. The intensity of scattering significantly increased with time in the whole frequency region towards the measuring limit of apparatus (Fig. 5).

Also, the intensity of Raman scattering of colloidal silver in H_2O significantly increased in a similar manner to

Table 1 Raman frequencies for the colloidal silver and gold (in cm^{-1})

$HAuCl_4$[a] D_2O	$AgClO_4$[b] D_2O	PEG[c]	S465[d]	mix.[e] H_2O	Ag sol[f] D_2O	Ag sol[g] H_2O	Ag sol[h] H_2O	Au sol[i] D_2O	Tentative assignment	Reference
354									Au–Cl stretching	18
		808	820	835				858	CH_2 rocking	19, 20
	935			935			930		Cl–O stretching	21
		1130	1139	1134					C–O,C–C stretching	19, 20
1206	1204								D_2O	
		1286	1286	1286				1303	CH_2 twist	19, 20
							1390		CH_3 deformation	
		1470	1463	1470				1469	CH_2 deformation	19, 20
					1534	1534	1546	1512	C=C stretching for	
									$\left[\begin{array}{c}\rangle C{=}C\langle \\ \vdots \\ Ag\end{array}\right]^+ ClO_4^-$ or	
									$\left[\begin{array}{c}\rangle C{=}C\langle \\ \vdots \\ Au\end{array}\right]^+ AuCl_4^-$	
				1627					H_2O	
				1769	1796	1796			C=O stretching	22, 23
					1960	1960	1970		C≡C stretching for	
									$\left[\begin{array}{c}-C{\equiv}C- \\ \vdots \\ Ag\end{array}\right]^+ ClO_4^-$	
			2229						C≡C stretching	22, 23
2515	2515							2515	D_2O	
		2875	2872	2945	2929	2933	2936	2933	CH_2, CH_3 stretching	22, 23

[a]: $HAuCl_4$ D_2O solution, [b]: $AgClO_4$ D_2O solution, [c]: PEG (neat), [d]: Surfynol 465 (neat), [e]: mixture of $AgClO_4$ and PEG in H_2O, [f]: colloidal D_2O solution of silver, [g]: colloidal H_2O solution of silver, [h]: colloidal H_2O solution of silver (resonance Raman spectrum), [i]: colloidal D_2O solution of gold.

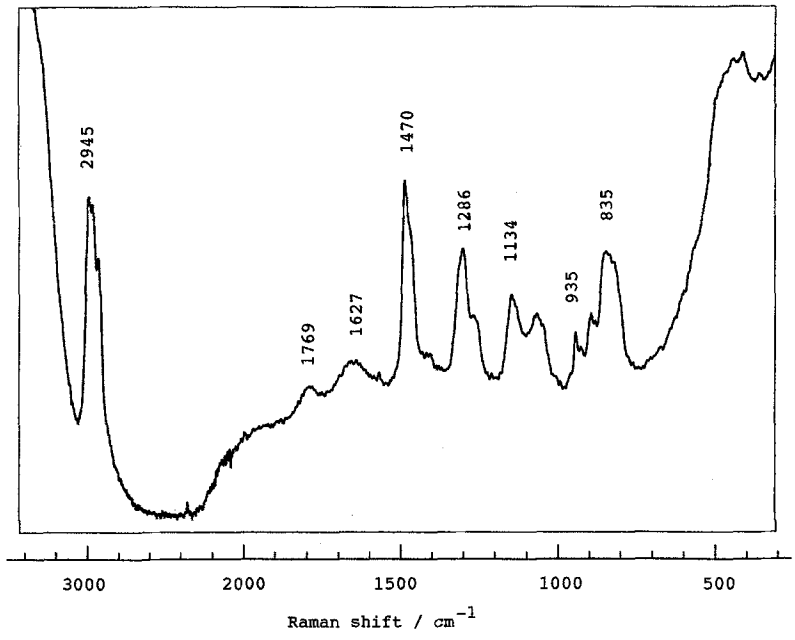


Fig. 4 FT-Raman spectrum of the mixture of equal volumes of two H_2O solutions of $AgClO_4$ (0.04 mol kg^{-1}) and polyethylene glycol (1 mol kg^{-1}). The output power of laser for excitation was 1 W

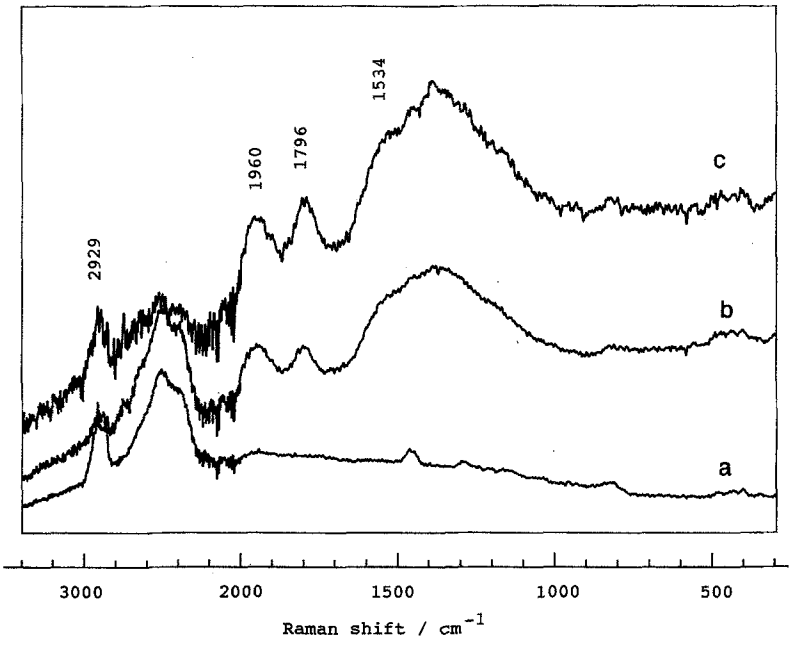


Fig. 5 FT-Raman spectra of the colloidal silver prepared from two D_2O solutions of $AgClO_4$ (0.04 mol kg^{-1}) and Surfynol 465 (0.8 mol kg^{-1}). The spectra were repeatedly measured on the same sample and shown in order of a), b) and c). a) colloidal silver, b) colloidal silver after irradiation for 2 min with a high output power of laser (200 mW), c) colloidal silver with silver mirror. The output power of laser for excitation was 100 mW

the case of colloidal silver in D_2O (Fig. 6). These anomalous behaviors of Raman scattering were observed when mirrors of silver were formed at the wall of capillary tube which was directly irradiated with the laser beam for excitation. Through the formation of silver mirrors the Raman spectra in Figs. 5 and 6 were correlated with the SERS on colloidal silver which could be observed when the silver particles aggregated with each other by the addition of adsorbed molecule such as pyridine and citrate [8, 9, 11–16].

With the formation of silver mirrors, new Raman bands were observed at around 1960, 1796 and 1534 cm^{-1} (Table 1). In the same manner as applied to the case of the mixture of $AgClO_4$ and PEG, the band at 1796 cm^{-1} could be assigned to the C=O stretching vibration of carbonyl compounds formed from two poly(oxyethylene) chains.

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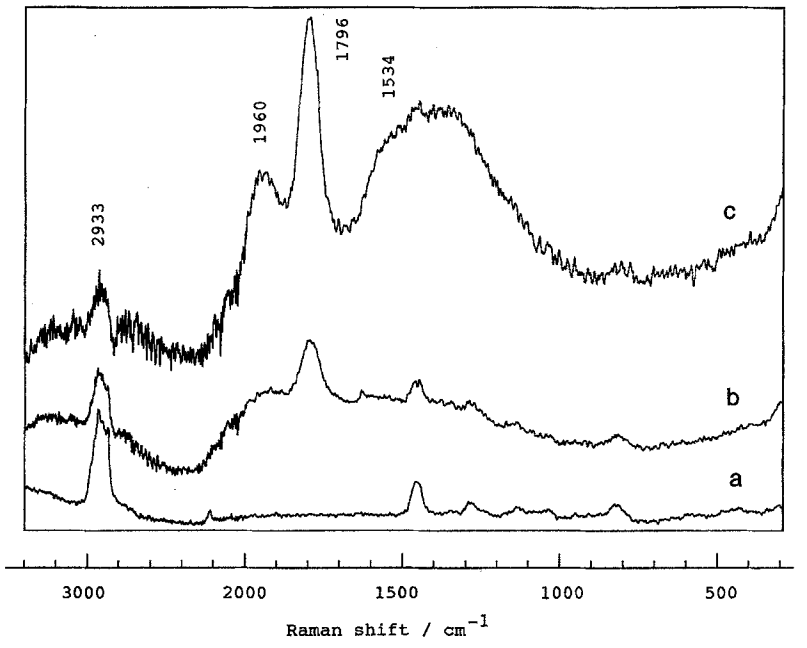

Fig. 6 FT-Raman spectra of the colloidal silver prepared from two H_2O solutions of $AgClO_4$ (0.04 mol kg^{-1}) and Surfynol 465 (0.8 mol kg^{-1}). The spectra were repeatedly measured on the same sample and shown in order of a), b) and c). a) colloidal silver, b) colloidal silver after irradiation for 19 min with a high output power of laser (200 mW), c) colloidal silver with silver mirror. The output power of laser for excitation was 100 mW

As for the band at 1534 cm^{-1}, although the shape was not clear, we discuss as follows. Generally, Ag^+ has a strong affinity for ethylene (>C=C<) or acetylene (–C≡C–) and tends to form a complex with it, which Mulliken et al. called molecular compound [27–29]. In the Raman spectra, adsorbed ethylene on silver surface gets the band at 1585 cm^{-1}, which is intermediate between two stretching frequencies for the C=C group of gaseous ethylene (1623 cm^{-1}) and the C–C group of gaseous ethane (993 cm^{-1}), supporting the formation of a complex between ethylene and Ag, i.e., $\left[\begin{smallmatrix}>C=C<\\ \vdots\\ Ag\end{smallmatrix}\right]^+$ [15, 30]. Then, the band observed at 1534 cm^{-1} might be assigned to the C=C stretching vibration for the complex, $\left[\begin{smallmatrix}>C=C<\\ \vdots\\ Ag\end{smallmatrix}\right]^+ ClO_4^-$. In the above discussion, we supposed that the functional group, >C=C<, was produced from –C≡C– of Surfynol 465 in the colloidal silver dispersion.

Also, it must be noted that the band at 1960 cm^{-1} is intermediate between two bands due to C≡C stretching vibration for R–C≡C–R′ (2301–2231 cm^{-1}) and C=C stretching vibration for cis-dialkyl ethylenes (1660–1654 cm^{-1}) [23]. If $AgClO_4$ and –C≡C– form the complex, $\left[\begin{smallmatrix}-C\equiv C-\\ \vdots\\ Ag\end{smallmatrix}\right]^+ ClO_4^-$, it might be said that the Raman band at 1960 cm^{-1} was due to the stretching vibration of C≡C for $\left[\begin{smallmatrix}-C\equiv C-\\ \vdots\\ Ag\end{smallmatrix}\right]^+ ClO_4^-$ in a similar manner to the case of $\left[\begin{smallmatrix}>C=C<\\ \vdots\\ Ag\end{smallmatrix}\right]^+ ClO_4^-$.

Resonance Raman scattering of colloidal silver

The resonance Raman scattering of the colloidal silver prepared from $AgClO_4$ and Surfynol 465 in H_2O was measured. When the excitation was provided with the 514.5 nm line of argon ion laser, we observed the formation of silver mirror and the Raman bands at 2936, 1970, 1546, 1390 and 930 cm^{-1} in Fig. 7, suggesting the surface enhanced resonance Raman scattering. On the basis of the results of FT-Raman scattering, each band could be assigned as follows. The band at 2936 cm^{-1} was due to the CH_2 and CH_3 stretching vibrations of hydrocarbon and poly(oxyethylene) chains in Surfynol 465. The band at 1970 cm^{-1} was due to the C≡C stretching vibration for $\left[\begin{smallmatrix}-C\equiv C-\\ \vdots\\ Ag\end{smallmatrix}\right]^+ ClO_4^-$. The band at 1546 cm^{-1} was due to the C=C stretching vibration for $\left[\begin{smallmatrix}>C=C<\\ \vdots\\ Ag\end{smallmatrix}\right]^+ ClO_4^-$. The band at 1390 cm^{-1} was due to the CH_3 deformation vibration of Surfynol 465. And the band at 930 cm^{-1} was due to the Cl–O stretching vibration of $AgClO_4$ (Table 1).

From the relation between two wavelengths of the absorption peak of colloidal silver and the laser provided for excitation, i.e., 405 and 514.5 nm, respectively, each band observed in the resonance Raman spectrum could be assigned to the corresponding functional group, which is a part of the adsorbed molecule and directly interacts with colloidal silver [31].

Then, on the basis of the results of FT-Raman and resonance Raman scatterings, a series of reactions for the

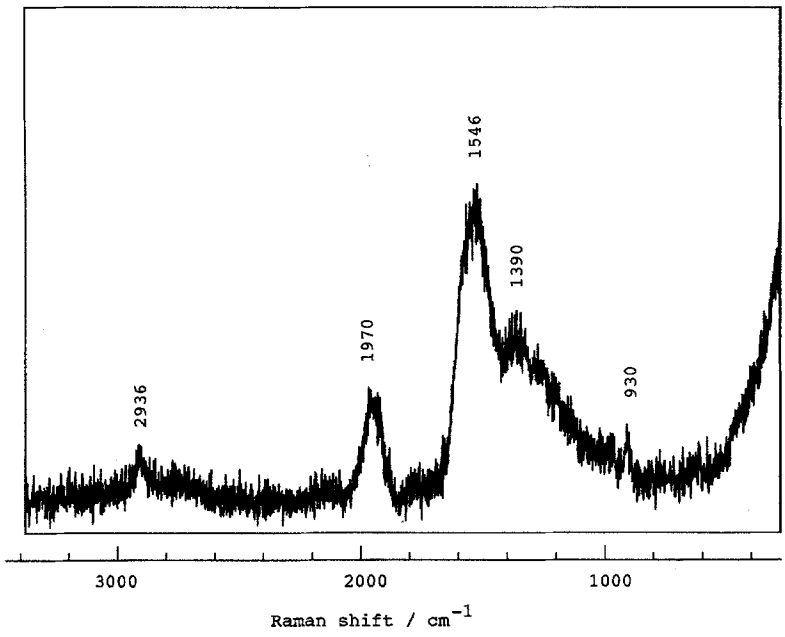

Fig. 7 Resonance Raman spectrum of the colloidal silver prepared from two H_2O solutions of $AgClO_4$ (0.04 mol kg^{-1}) and Surfynol 465 (0.8 mol kg^{-1}). The output power of laser for excitation was 140 mW

formation of colloidal silver in aqueous media was proposed.

$$-C\equiv C- + AgClO_4 \longleftrightarrow \begin{bmatrix} -C\equiv C- \\ \vdots \\ Ag \end{bmatrix}^+ ClO_4^-, \quad (2)$$

$$\begin{bmatrix} -C\equiv C- \\ \vdots \\ Ag \end{bmatrix}^+ ClO_4^- + AgClO_4 + 4\ -CH_2OCH_2- \longrightarrow -CCl=CCl- + 2Ag(0) + 4\ -CH(OOH)OCH_2-, \quad (3)$$

$$-CCl=CCl- + AgClO_4 \longleftrightarrow \begin{bmatrix} -CCl=CCl- \\ \vdots \\ Ag \end{bmatrix}^+ ClO_4^-, \quad (4)$$

and

$$\begin{bmatrix} -CCl=CCl- \\ \vdots \\ Ag \end{bmatrix}^+ ClO_4^- + AgClO_4 + 4\ -CH_2OCH_2- \longrightarrow -CCl_2-CCl_2- + 2Ag(0) + 4\ -CH(OOH)OCH_2-, \quad (5)$$

where Ag(0) is an atomic silver and $-CH_2OCH_2-$ is related to the polyoxyethylene chains of Surfynol 465. From Eqs. (3) and (5),

$$m\mathrm{Ag}(0) \rightarrow \text{a silver fine particle}, \quad (6)$$

where m is the number of silver atom forming the fine particle.

Thus, from the results of FT-Raman and resonance Raman scatterings, it was suggested that the CH_3 and CH_2 groups of Surfynol 465 and ClO_4^- of $AgClO_4$ were adsorbed on the surface of silver particle, and the $-C\equiv C-$ or $>C=C<$ group of Surfynol 465 formed a complex with Ag^+ or Ag(0). Two poly(oxyethylene) chains of Surfynol 465 surrounding the silver particle prevent it from aggregation with each other as protecting agents, although there was also an electrostatic repulsive action due to the charge of particle [32].

FT-Raman scattering of colloidal gold

The Raman scattering for the mixture of $HAuCl_4$ and PEG in D_2O or H_2O was measured. All Raman bands in the spectrum were assigned to $HAuCl_4$ and PEG. We could not have any Raman bands around 1700 cm^{-1}, which were due to the C=O stretching vibration of aldehydes observed at the mixture of $AgClO_4$ and PEG in H_2O mentioned above. Thus, it was found that the autooxidation and the degradation of PEG did not undergo in $HAuCl_4$ aqueous solution.

Next, the FT-Raman scattering of colloidal gold prepared from two aqueous solutions of $HAuCl_4$ and Surfynol 465 was measured. The FT-Raman spectrum of colloidal gold depended on the output power of laser for excitation in a similar manner to the case of colloidal silver. When the gold mirrors were formed, we found the Raman scattering with anomalous intensity, suggesting the SERS on colloidal gold [8, 9, 12]. Consequently, in

addition to the bands of $HAuCl_4$ and Surfynol 465 a new Raman band was observed at 1512 and 1507 cm^{-1} in D_2O and H_2O, respectively (Fig. 8).

Also, $HAuCl_4$ can form the complex with $\rangle C{=}C\langle$, $\left[\begin{matrix}\rangle C{=}C\langle \\ \vdots \\ Au\end{matrix}\right]^+ AuCl_4^-$, and the complex with $-C{\equiv}C-$, $\left[\begin{matrix}-C{\equiv}C- \\ \vdots \\ Au\end{matrix}\right]^+ AuCl_4^-$ [33, 34]. It is noted that Au^{3+} is reduced to Au^+ on the formation of the complexes. And furthermore, Kasai has reported that $HAuCl_4$ forms the complex with $-C{\equiv}C-$ by the studies on ESR [35].

Meanwhile, the colloidal gold is characterized by its wine red color, corresponding to the absorption peak around 530 nm in the UV-VIS spectrum [36]. If $HAuCl_4$ aqueous solution was mixed with Surfynol 465 aqueous solution, we could observe by the naked eye the color change of mixture from pale yellow to wine red through the colorless intermediate with time. As Surfynol 465 has no color, the color of mixture was considered to mainly depend on the state of electric charge of gold. The pale yellow is due to Au^{3+}, and the wine red is from an atomic gold, Au(0). To the intermediate without color, we could apply Au^+ on the basis of the results of other studies [33, 34, 37, 38]. Thus, from the color change of mixture of $HAuCl_4$ and Surfynol 465 with time, it was also suggested that Au^{3+} was gradually reduced to Au^+ and Au(0) through the formation of the complex.

It is noted that in the same manner as the case of colloidal silver, the two complexes without color, $\left[\begin{matrix}-C{\equiv}C- \\ \vdots \\ Au\end{matrix}\right]^+ AuCl_4^-$ and $\left[\begin{matrix}\rangle C{=}C\langle \\ \vdots \\ Au\end{matrix}\right]^+ AuCl_4^-$, are very important for the formation of colloidal gold. Here, the $\rangle C{=}C\langle$ group was considered to be produced from the $-C{\equiv}C-$ group of Surfynol 465 through $\left[\begin{matrix}-C{\equiv}C- \\ \vdots \\ Au\end{matrix}\right]^+ AuCl_4^-$.

Then, the Raman band at 1512 cm^{-1} in Fig. 8 was assigned to the C=C stretching vibration of $\left[\begin{matrix}\rangle C{=}C\langle \\ \vdots \\ Au\end{matrix}\right]^+ AuCl_4^-$. However, the Raman band for the $-C{\equiv}C-$ stretching vibration of $\left[\begin{matrix}-C{\equiv}C- \\ \vdots \\ Au\end{matrix}\right]^+ AuCl_4^-$ was not found around 1960 cm^{-1}, showing that $\left[\begin{matrix}-C{\equiv}C- \\ \vdots \\ Au\end{matrix}\right]^+ AuCl_4^-$ was too unstable to follow the $-C{\equiv}C-$ stretching vibration in the measurement of FT-Raman scattering [33, 34].

From these results, a series of reactions for the formation of colloidal gold in the presence of Surfynol 465 was proposed, as follows.

$$-C{\equiv}C- + 2\,HAuCl_4 \longleftrightarrow \left[\begin{matrix}-C{\equiv}C- \\ \vdots \\ Au\end{matrix}\right]^{3+} AuCl_6^{3-} + 2\,HCl, \quad (7)$$

$$\left[\begin{matrix}-C{\equiv}C- \\ \vdots \\ Au\end{matrix}\right]^{3+} AuCl_6^{3-} \longrightarrow \left[\begin{matrix}-C{\equiv}C- \\ \vdots \\ Au\end{matrix}\right]^{+} AuCl_4^- + Cl_2, \quad (8)$$

$$\left[\begin{matrix}-C{\equiv}C- \\ \vdots \\ Au\end{matrix}\right]^{+} AuCl_4^- \longrightarrow -CCl{=}CCl- + 2\,Au(0) + Cl_2, \quad (9)$$

and

$$n\,Au(0) \rightarrow \text{a gold fine particle}, \quad (10)$$

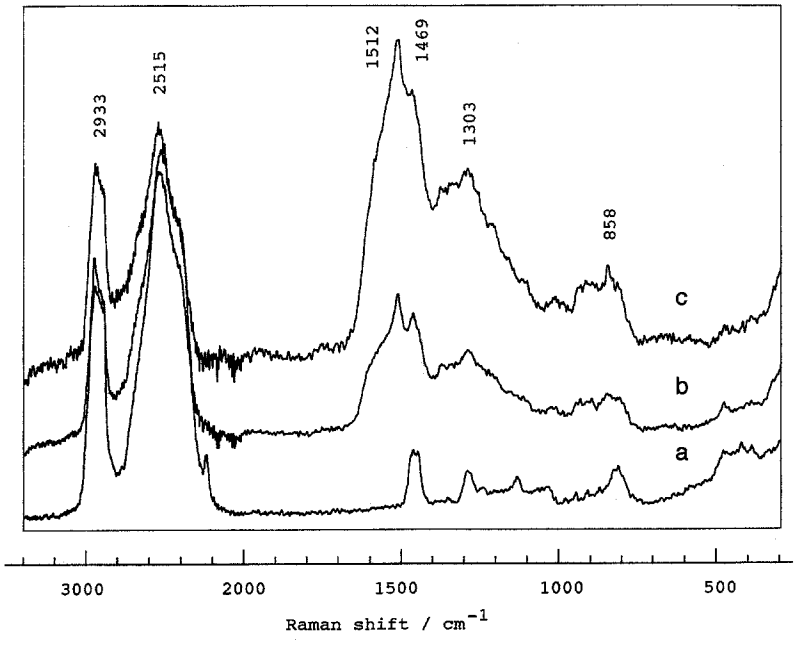

Fig. 8 FT-Raman spectra of the colloidal gold prepared from two D_2O solutions of $HAuCl_4$ (0.01 mol kg^{-1}) and Surfynol 465 (1 mol kg^{-1}). The spectra were repeatedly measured on the same sample and shown in order of a), b) and c). a) colloidal gold, b) colloidal gold after irradiation for 1 min with a high output power of laser (1 W), c) colloidal gold with gold mirror. The output power of laser for excitation was 200 mW

where n is the number of atomic gold forming a fine particle. Through the formation of complex, Au^{3+} is finally reduced to Au(0) and the –C≡C– group of Surfynol 465 is oxidized to the –CCl=CCl– group.

Furthermore, the –CCl=CCl– group produced from Surfynol 465 will be oxidized to the $-CCl_2-CCl_2-$ group through the formation of the complex with $HAuCl_4$, $\left[\begin{array}{c}-CCl=CCl-\\ \vdots \\ Au\end{array}\right]^+ AuCl_4^-$, in a similar way to that –C≡C– does.

Surfynol 465 in the colloidal silver or gold

In the formation of the colloidal silver or gold in the presence of Surfynol 465, the concentration of Surfynol 465 was very high in compared with that of $AgClO_4$ or $HAuCl_4$. If a series of reactions for the formation of colloidal silver or gold, mentioned above, is acceptable, all $AgClO_4$ or $HAuCl_4$ would be perfectly reduced to atomic silver or gold to form the silver or gold fine particles. Only a few –C≡C– groups of Surfynol 465 would be oxidized to the –CCl=CCl– and $-CCl_2-CCl_2-$ groups, and most of Surfynol 465 did not change.

Macromolecules such as proteins, polysaccharides and various synthetic polymers protect the gold fine particles from subsequent aggregation by an adsorption on their surface [32]. The results of the SERS on colloidal silver or gold indicated that ethylene oxide groups of Surfynol 465 located near the particle surface of silver or gold. Thus, Surfynol 465, which did not contribute to the reaction, was considered to function as a protecting agent of colloidal silver or gold formed as well as a reducing agent of $AgClO_4$ or $HAuCl_4$.

Consequently, on the basis of the SERS spectra observed with the formation of silver or gold mirror, we could examine the reaction mechanism for the formation of colloidal silver or gold in the presence of Surfynol 465.

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