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Preparation of Nonmetallic Silver Clusters in Aqueous Solutions Using UV Lasers

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Nonmetallic silver clusters (λ_{max} = 275 nm) were *prepared* by UV laser irradiation of aqueous solutions of silver perchlorate in the presence of 2-propanol and sodium polyphosphate. They were transformed into silver colloids (λ_{max} = 380 nm) obeying second-order kinetics. Effects of added electrolytes on the kinetics were studied.

Radiolytic formation of nonmetallic silver clusters has been reported by Henglein's group[1-5] and Belloni's group.[6,7] Henglein[1,2] reduced silver ions in aqueous solutions of silver perchlorate containing alcohol and stabilizers such as sodium polyphosphate (SPP), using γ-rays of a ^{60}Co source. An absorption band at 275 nm developed initially. Upon further irradiation this band disappeared and two bands at 300 and 325 nm showed up, together with the 380 nm-band of metallic silver colloids. The bands below 380 nm were attributed to nonmetallic silver clusters. Mulvaney and Henglein[3] proposed the mechanism:

$$Ag^0 + Ag^+ \rightarrow Ag_2^+ \quad (1)$$

$$2Ag_2^+ \rightarrow Ag_4^{2+} \quad (2)$$

Initially formed Ag_2^+ (λ_{max} = 310 nm) dimerized into Ag_4^{2+} (λ_{max} = 275 nm). Linnert et al.[4] reported the formation of larger clusters with absorption bands at 300, 330 and 345 nm in the later stages of Ag^+ reduction using a ^{60}Co source. They reported *photolysis* of these clusters by 308-nm light pulses of an excimer laser, resulting in larger particles of quasi-metallic (λ_{max} = 360 nm) and metallic (λ_{max} = 380 nm) silver.

In the present paper, UV laser (193 or 248 nm) pulses were used in the *preparation* of silver clusters. The 275-nm band of silver clusters was observed. Its transformation into metallic colloidal silver (λ_{max} = 380 nm) was found to obey second-order kinetics. Effects of added electro-

lytes on their kinetics were studied.

Silver perchlorate, SPP, 2-propanol, perchloric acid, sodium perchlorate, sodium sulfate, and pottassium sulfate (Nacalai Tesque) were used as received. Water was distilled twice.

Degassed aqueous solutions of silver perchlorate containing 2-propanol and a stabilizer (SPP) were irradiated with unfocused 193-nm or 248-nm light pulses of a Lambda Physik LPX-105 excimer laser. Laser power was monitored by a Scientech 38-2UVS laser power meter. Absorption spectra and absorption decay were measured on a Hitachi 200-20 double-beam spectrophotometer, using a temperature-controled jacketted cell. Digital output of the spectrophotometer was fed to a microcomputer.

Absorption spectra of aqueous solutions containing 1.0×10^{-3} M (1 M = 1 mol dm^{-3}) of sodium perchlorate, 5.0×10^{-4} M of SPP and 0.10 M of 2-propanol, measured after UV laser irradiation at 193 nm (30 mJ $pulse^{-1}$, 5 Hz, 300 pulses) are shown in Fig. 1. Temperature of the solution was 27 °C. The band at 275 nm was observed immediately after irradiation. Its position is in accordance with the band of Ag_4^{2+} reported by Henglein et al.[1,2] UV laser irradiation at 248 nm (216 mJ $pulse^{-1}$, 5 Hz, 200 pulses) gave similar results. Thus, silver clusters were *prepared* by UV laser irradiation. This is the first report of direct preparation of silver clusters in aqueous solutions by UV laser irradiation, to the best of our knowledge.[8]

Henglein[1,2] explained radiolytic formation of Ag^0 by reduction of Ag^+ by hydrated electrons and by organic radicals formed on the reaction of ·OH (from $H_2O \rightarrow e_{aq}^- + H^+ + \cdot OH$) and alcohol. Although two-photon ionization of liquid water to give hydrated electrons by UV laser irradiation was reported,[9] two-photon process is not likely in the present case, because focusing of laser light did not lead to increase

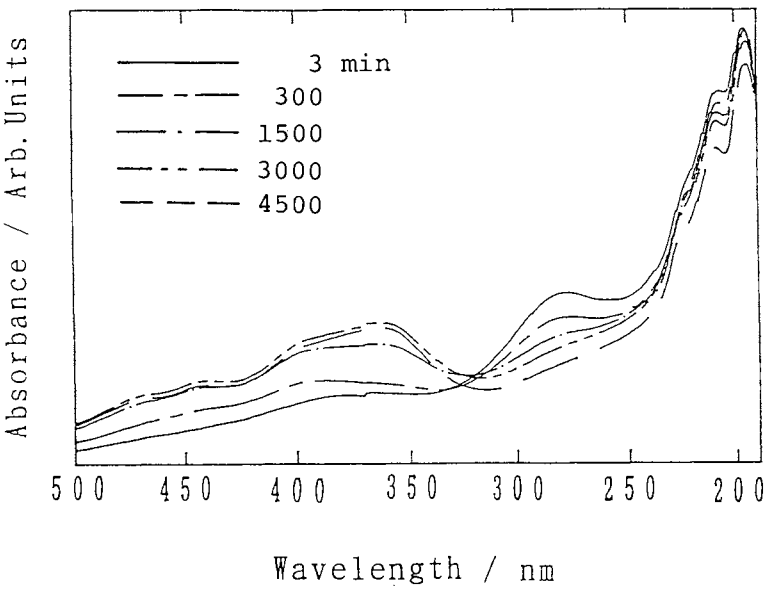

Fig. 1. Absorption spectra of aqueous solutions on 193-nm laser excitation (see Text). The time after irradiation was stopped (min) is shown in the figure. Temperature: 27 °C.

of silver clusters. Hada et al.[10] reported that irradiation of an $AgClO_4$ solution with 253.7 nm light induced one-photon photo-oxidation of H_2O by excited Ag^+, resulting in the formation of Ag^0, H^+ and ·OH. The reduction of Ag^+ in the present case seems to occur in the similar way.

It is to be noted that the silver clusters are remarkably long-lived; the 275-nm band was observable even after a day. This is in contrast to the lifetime from minutes to hours observed by Henglein et al. [1,3]

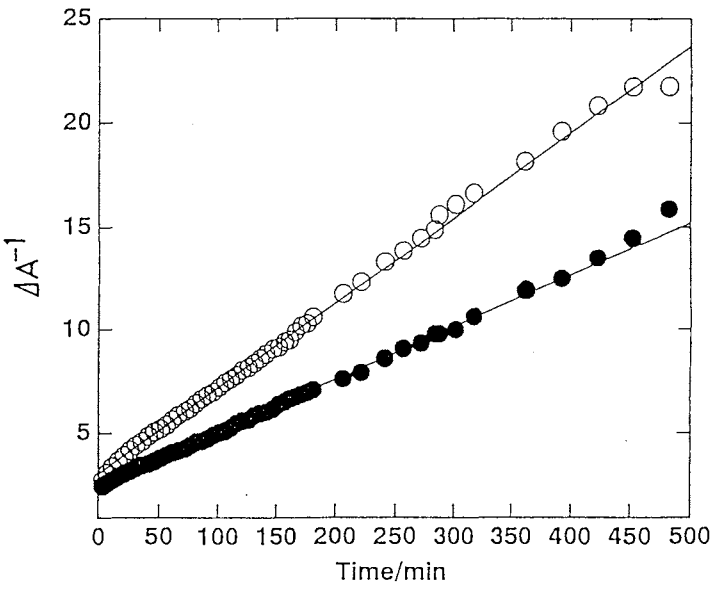

Fig. 2. Reciprocals of $\Delta A = |A(t)-A(\infty)|$ vs. time. Concentrations of reagents are the same to those in Fig. 1. 193-nm excitation, ○ 275 nm, ● 380 nm, temperature: 50 °C.

The intensity of the 275-nm band decreased with time, with the concomitant increase of the 380-nm band intensity. Reciprocals of absorbance, $\Delta A(t) = |A(t)-A(\infty)|$, at these wavelengths are plotted against time, as exemplified in Fig. 2. The decay of silver clusters and the build-up of silver colloids were found to obey second-order kinetics. Apparent second-order rate constants for three temperatures are shown in Table 1. Although "oligomeric" clusters absorbing at wavelengths between 275 and 380 nm were reported by Linnert et al.,[4] none of these bands were discerned in the present study.

Table 1. Apparent second-order rate constants (absorbance^{-1} s^{-1}), $AgClO_4$:1.0×10^{-3} M, sodium polyphosphate:5.0×10^{-4} M, 2-propanol:0.1 M, 193-nm irradiation

Temp (°C)	Decay of clusters (at 275 nm)	Build-up of colloids (at 380 nm)
27.5	2.54×10^{-4}	1.82×10^{-4}
40	2.40×10^{-2}	1.39×10^{-2}
50	4.11×10^{-2}	2.54×10^{-2}

Mulvaney and Henglein[3] reported that Ag_4^{2+} is stabilized by strong binding to SPP, preventing further reaction to form larger clusters. We studied effects of added electrolytes (perchloric acid, sodium perchlorate, sodium sulfate, or pottasium sulfate) on the stability of Ag_4^{2+}. When one of these electrolytes (0.1 M) was added to the initial solution ($AgClO_4$: 1.0×10^{-3} M, SPP: 5.0×10^{-4} M, 2-propanol: 0.1 M), the 275-nm band

appeared only as a shoulder, and the 380-nm band built up immediately after the 193-nm irradiation; addition of these electrolytes tremendously accelerated the conversion of clusters into colloids. Second-order rate constants for decay of the 275-nm band and build-up of the 380-nm band (27 °C) are plotted as a function of concentration of sodium perchlorate in Fig. 3. Nearly quadratic dependence was found for both, indicating a kinetic salt effect as reported by Ershov et al.[11] only for the band of Ag_4^{2+} (which appeared at 265 nm in the absence of a stabilizer).

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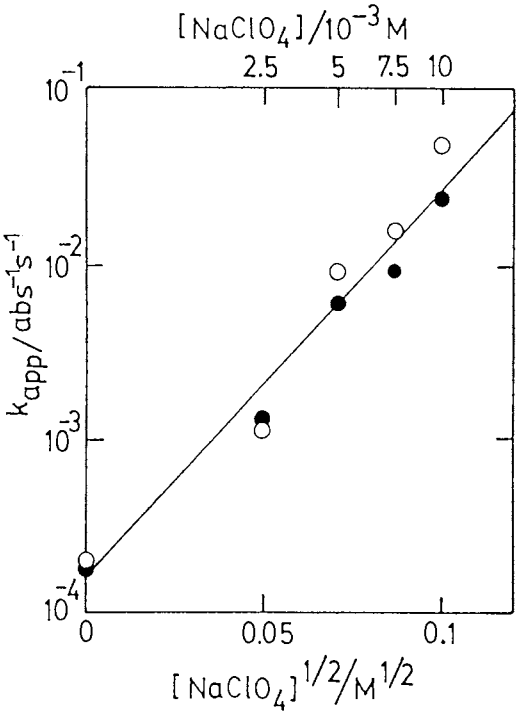

Fig. 3. Dependence of apparent second-order rate constants k_{app} (absorbance^{-1} s^{-1}) on $NaClO_4$ concentrations (27 °C, see Text). ○ decay of 275-nm band, ● build-up of 380-nm band.

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