

## Formation of Metal Particles and Thin Films by Photolysis of Metal Salts of Polysaccharide Derivatives

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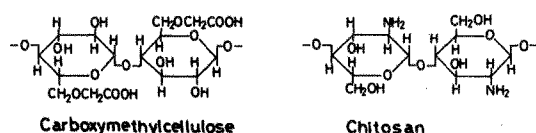
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Fabrication of metal particles and thin films by using carboxymethylcellulose (CMC) or chitosan (CTO) as the polymer support has been investigated. When the film of silver salt of CMC was irradiated with UV light in wet air at room temperature, the formation of a clear silver mirror was observed. Similarly, a clear gold mirror was formed when the film of chloroauric acid salt of CTO was photolyzed. With aids of UV-visible absorption spectroscopy, XRD, and scanning electron microscopy, it was found that the clear silver or gold mirror is made of aggregated colloidal metal particles stabilized by CMC or CTO. On the other hand, either small silver or gold clusters were formed when photolysis was carried out at low temperature in vacuum. It is suggested that metal atoms and clusters are capable of diffusing in the film at room temperature in air.

Key words: metal nanoparticle, photolysis, mirror, polysaccharide, polymer film

### 1. INTRODUCTION

On the way to the exploration of raw materials useful for industrial purposes, renewed interest in naturally occurring polymers has arisen because of their compatibility with environments. Cellulose and chitin are biosynthetic products which are formed by  $\beta$ -D-glucopyranose and *N*-acetyl- $\beta$ -D-glucopyranose units linked together by (1-4) glycosidic bonds. Chitin has identical structure with cellulose except that the secondary hydroxyl group on the  $\alpha$ -carbon atom is substituted with an acetamide group and plays the same skeletal role in arthropods as cellulose does in plants. Partial carboxymethylation of cellulose gives rise to carboxymethylcellulose (CMC) [1]. Chitosan (CTO) is the deacetylated product of chitin [2]. CMC and CTO, typical derivatives of cellulose and chitin, are anionic and cationic polyelectrolyte soluble to water and various acidic solvents, respectively. Schematic structure of CMC and CTO are shown in Scheme.



Scheme

Recently, complexation of CMC and CTO with metal ions has attracted attention [3]. When films of CMC and CTO are immersed in certain metal salt solutions, water-insoluble films are formed. As CMC and CTO are available for the protective agent of colloidal metal particles in solutions [4], they are

relevant to the fabrication of thin metal films by using those materials as the polymer support. We have found the formation of a clear silver mirror by photolysis of silver salt of alginic acid, a typical polysaccharide produced by brown algae [5]. In this study, we have taken up thin films of silver salt of CMC (CMC<sub>Ag</sub> film) and chloroauric acid salt of CTO (CTO<sub>Au</sub> film).

### 2. EXPERIMENTAL

A 0.5 wt.% aqueous solution of sodium salt of CMC (CMCNa<sup>+</sup>) (nacalai tesque Co., Daicel Chem. Ind. Ltd.) was prepared and spread on the quartz plate (10×30×1 mm<sup>3</sup>) by the amount of 0.05 ml/cm<sup>2</sup>. The CMCNa<sup>+</sup> film was dried and then immersed in 0.1M (1M=1 mol·dm<sup>-3</sup>) AgNO<sub>3</sub> aqueous solution for 0.5–1h to substitute Na<sup>+</sup> with Ag<sup>+</sup> ions. The film was washed with distilled water and dried again in the dark. The CMC<sub>Ag</sub> film was colourless and transparent. A 0.5 wt.% aqueous solution of CTO (Wako Chemicals Co.) in 1 vol% acetic acid was spread on the quartz plate (10×30×1 mm<sup>3</sup>) by the amount of 0.05 ml/cm<sup>2</sup>. The CTO film was dried and then immersed in 0.01M HAuCl<sub>4</sub> aqueous solution for 0.5–1h to form AuCl<sub>4</sub><sup>-</sup> salt. After washing with distilled water and drying in the dark, the light-yellow and transparent CTO<sub>Au</sub> film was formed. Cooling of the CTO film, HAuCl<sub>4</sub> solution and distilled water by ice was helpful to prepare high-quality CTO<sub>Au</sub> films. The thickness of the CMC<sub>Ag</sub> film and the CTO<sub>Au</sub> film was 1–5 μm.

The CMC<sub>Ag</sub> film on the quartz plate was exposed to 253.7 nm light from a 15 W sterilization lamp (Toshiba Co.) in the reaction chamber with controlled temperature for 15–25°C and relative humidity more than 70%. As the quality of thin gold films was sensitive to reaction

conditions, we had to pay special attention to temperature and humidity during photolysis of the CTOAu film. Relative humidity and temperature in the reaction chamber were controlled to be 70–85% and more than 20°C, respectively. We should note that a clear gold mirror was not formed at temperature below 20°C and humidity more than 85%.

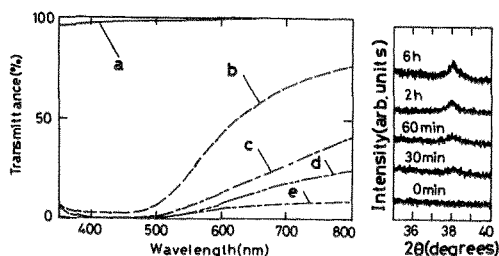
To estimate the amount of unreacted metal ions and the amount of deposited metal, atomic absorption spectrometry was employed by using a Hitachi Z-6100 spectrophotometer. The amount of  $\text{Ag}^+$  ions per  $1 \text{ cm}^2$  before photolysis was  $0.64 \mu\text{mol}/\text{cm}^2$  in the CMCAG film. That of  $\text{AuCl}_4^-$  ions in the CTOAu film was  $1.18 \mu\text{mol}/\text{cm}^2$ .

Transmittance spectra of the films were recorded on a UV-2200 spectrophotometer (Shimadzu Co.). The morphology of the films was examined by a high-resolution scanning electron microscope of the field emission type, Hitachi Model S-900. The x-ray diffraction (XRD) data were collected on a Shimadzu XD-610 with a  $\text{CuK}\alpha$  radiation.

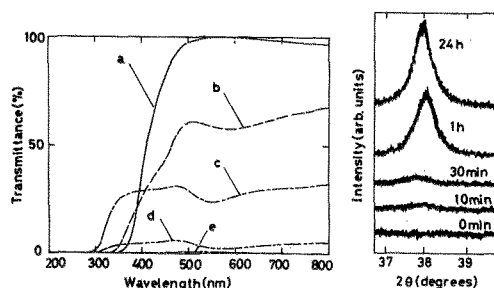
### 3. RESULTS

#### 3.1 Photolysis of CMCAG films

On irradiating with UV light in wet air at room temperature, the CMCAG film became yellow-brown colored due to the formation of colloidal silver. When irradiation was continued, the irradiated surface of the film gradually assumed metallic luster and finally changed into a clear silver mirror. Variation of transmittance spectra with irradiation is given in Fig. 1(A). The colloidal absorption band of silver which was located at  $\lambda=400\text{--}410 \text{ nm}$  developed with irradiation time. Finally, almost continuous absorption of the silver



(A)



(B)

Fig. 1 Variations of transmittance spectra and XRD profiles for the CMCAG film (A) and the CTOAu film (B) with UV irradiation.

(A) a; 0 min, b; 10 min, c; 30 min, d; 1 h, e; 24 h.

(B) a; 0 min, b; 20 min, c; 40 min, d; 1 h, e; 2 h.

metal film was observed. The XRD profile of the irradiated film is added to Fig. 1(A). After 6h photolysis, the diffraction line of the (111)face of the f.c.c. silver lattice is evident (JCPDS card 4-0783(Ag)). A broad diffraction line after 30 min irradiation indicates the formation of colloidal silver particles.

The dependence of the amount of photolytic silver ( $\Delta N_{\text{Ag}}$ ) on irradiation time is given in Fig. 2. It is shown that  $\Delta N_{\text{Ag}}$  was increased with irradiation time and became almost constant after 3h. The conversion efficiency of  $\text{Ag}^+$  ions at this stage was about 64%. A scanning electron micrograph of the CMCAG film after UV irradiation is shown in Fig. 3(A). Before irradiation, the surface of the CMCAG film looked fairly smooth. After 10h irradiation, the surface was densely covered with colloidal silver particles of several 10 nm size.

#### 3.2 Photolysis of CTOAu films

When the CTOAu film was irradiated with UV light in wet air at room temperature, the film first became blue-violet colored due to the formation of colloidal gold.

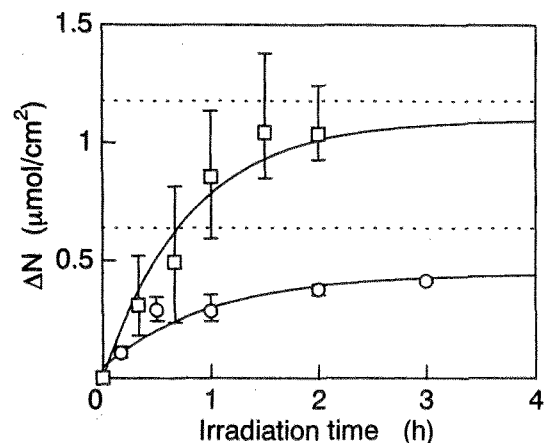


Fig. 2 Growth of the amount  $\Delta N$  of deposited silver (circle) and gold (square) with UV irradiation.  $\Delta N$  ( $\mu\text{mol}/\text{cm}^2$ ) is given per square centimetre of the film.

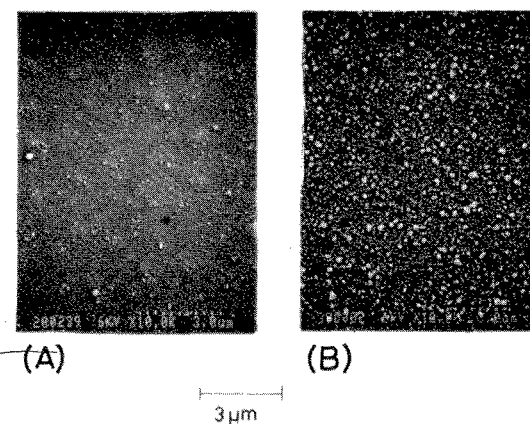


Fig. 3 Scanning electron micrographs of the CMCAG film (A) and CTOAu film (B) after photolysis.

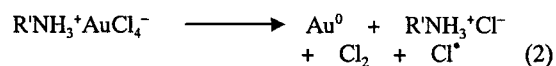
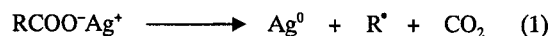
(A) 10 h irradiation, (B) 2 h irradiation.

After a prolonged irradiation, the irradiated surface changed into a clear gold mirror. Variation of transmittance spectra with irradiation is given in Fig. 1(B). The absorption spectrum of the CTOAu film before irradiation was characterized by absorption shorter than  $\lambda=320$  nm due to ligand-to-metal charge transfer (LMCT) band [6]. On irradiation, the LMCT band was decreased and the colloidal absorption band of gold at  $\lambda=540$ – $560$  nm developed. The colloidal absorption band got broader and finally, almost continuous absorption of the gold metal film was observed. The XRD profile of the irradiated film is added to Fig. 1(B). After 1h photolysis, diffraction line of the (111) face of the f.c.c. gold lattice is evident (JCPDS card 4-0784(Au)). Photolytic gold after 24h irradiation is in a highly crystalline state.

The dependence of the amount of photolytic gold ( $\Delta N_{Au}$ ) on irradiation time is included in Fig. 2. Apart from relatively large errors, it appeared that  $\Delta N_{Au}$  was increased with irradiation time and became almost constant after 1.5h. The conversion efficiency of  $AuCl_4^-$  ions at this stage was about 88%. A scanning electron micrograph of the CTOAu film is shown in Fig. 3(B). After photolysis for 2h, the surface was densely covered with colloidal gold particles (10–100 nm size).

#### 4. DISCUSSION

Preparation of precious metal particles by reducing metal salts has been studied extensively [7]. Recently, chemical reduction of  $Ag^+$  and  $AuCl_4^-$  in the presence of chitosan [4] and imogolite [8] has been reported. We have focussed on photoreduction method because of the flexibility of reaction conditions [9]. Overall photochemical reactions in the CMCAg film and the CTOAu film are expressed as:



In these films, silver atoms ( $Ag^0$ ) or gold atoms ( $Au^0$ ) initially formed at the  $Ag^+$  ion or  $AuCl_4^-$  ion site migrate and yield small metal clusters,  $Ag_n$  or  $Au_n$ , composed of several atoms. At room temperature in air, metal atoms and small clusters could diffuse in the film and aggregate themselves, forming large metal clusters and colloidal particles. Finally, these small particles aggregate at the irradiated surface, giving rise to either silver or gold mirror.

It is likely that evacuation and low temperature can suppress migration of metal atoms and clusters. We have examined photolysis of the CMCAg film at 77K in vacuum. The film was set in the cryostat and irradiated through the quartz window with 253.7 nm light from a 200 W low-pressure mercury lamp (Ushio Denki Co.). Variation of absorption spectra of the CMCAg film with irradiation is shown in Fig. 4. The 4h irradiation at 77 K resulted in the broad absorption in the  $\lambda=200$ – $600$  nm range, together with a shoulder around  $\lambda=330$  nm. Such spectrum is considerably different from that obtained when the film was photolyzed at room temperature in air. The film was heated until room temperature and kept in vacuum in the dark. In consequence, peaks at  $\lambda=300$ nm,

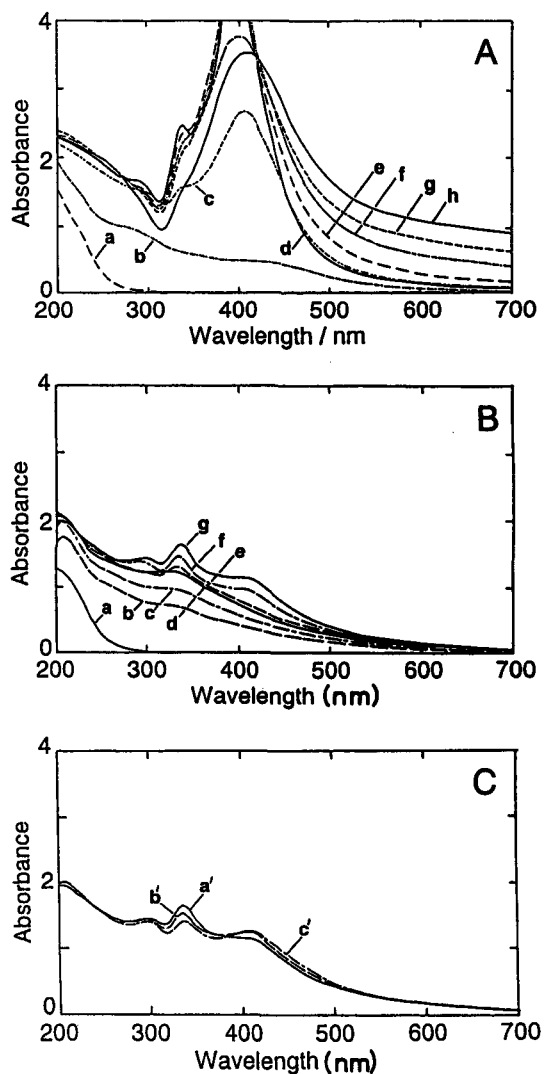


Fig. 4 Variation of absorption spectra of the CMCAg film with UV irradiation.

A Irradiation at room temperature in air. Irradiation time a; 0 min, b; 1 min, c; 5 min, d; 30 min, e; 1.5 h, f; 3 h, g; 5 h, h; 10 h.

B Irradiation at liquid nitrogen temperature in vacuum (a–d), followed by dark storage in vacuum at room temperature (e–g). Irradiation time a; 0 min, b; 1 h, c; 2 h, d; 4 h. Dark storage time after 4 h irradiation e; 30 min, f; 1 h, g; 20 h.

C After introduction of air to sample B and dark storage at room temperature. Dark storage time a'; 0 min, b'; 5 min, c'; 10 h.

335 nm and the colloidal absorption band of silver at  $\lambda=400$ – $410$  nm appeared. After introduction of air, a slight decrease of the 335 nm peak and an increase of the colloidal absorption band were noticed. It is reasonable that peaks at  $\lambda=300$  nm and 335 nm are assigned to certain silver clusters stabilized in the polymer matrix [10,11]. We have also photolyzed the CTOAu film at 77K in vacuum. Irradiation for 2h did not yield any definite peaks. However, when the film was heated to room temperature and subjected to air, the colloidal absorption band of gold at  $\lambda=530$ – $540$  nm was

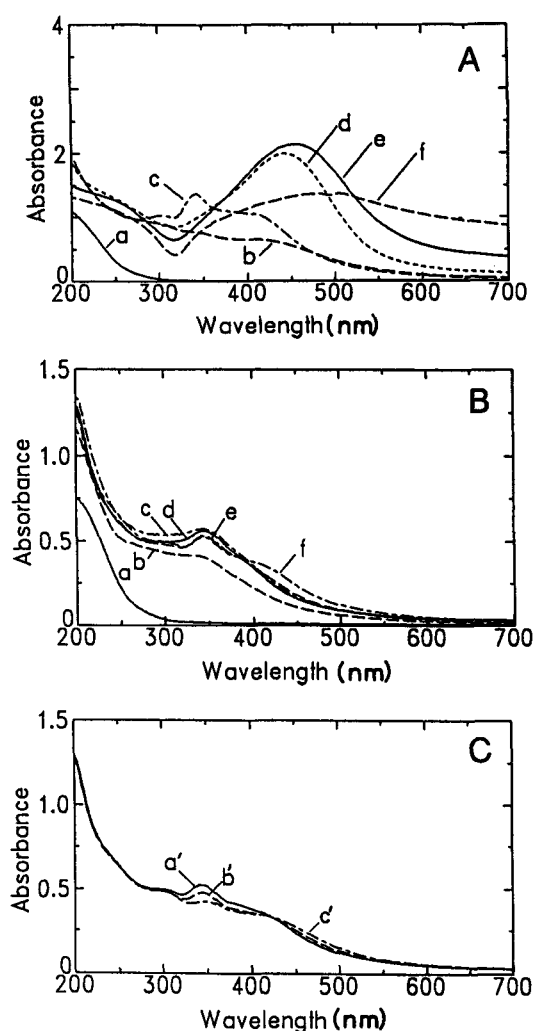


Fig. 5 Variation of absorption spectra of the PMAAg film with UV irradiation.

A Irradiation at room temperature in air. Irradiation time a; 0 min, b; 2 min, c; 10 min, d; 3 h, e; 10 h, f; 40 h. B Irradiation at liquid nitrogen temperature in vacuum (a—c), followed by dark storage in vacuum at room temperature (d—f). Irradiation time a; 0 min, b; 1 h, c; 4 h. Dark storage time after 4 h irradiation d; 30 min, e; 1 h, f; 20 h. C After introduction of air to sample B and dark storage at room temperature. Dark storage time a'; 0 min, b'; 1 h, c'; 10 h.

observed. Accordingly, it is plausible that the main products at low-temperature photolysis are gold atoms and clusters stabilized in the CTO matrix [12].

We have so far examined photolysis of metal salts of polysaccharide derivatives, CMC and CTO. The silver salt of polymethacrylic acid (PMA) is interesting because of considerably different structure of the monomer unit. Thin film of silver salt of polymethacrylic acid (PMAAg film) was fabricated from polymethacrylic acid (Scientific Polymer Products Inc.) and photolyzed. Variation of absorption spectra of the PMAAg film with irradiation is given in Fig. 5. In this film, a peak at  $\lambda=345$  nm, probably due to certain

silver clusters, appeared after 10 min irradiation at room temperature in air. Prolonged irradiation caused the development of the colloidal absorption band at  $\lambda=440$ – $450$  nm, along with the decrease of the 345 nm peak. Irradiation more than 40h yielded a silver mirror. On the other hand, photolysis at 77 K in vacuum resulted in broad structureless absorption ( $\lambda=200$ – $600$  nm), together with a peak around  $\lambda=345$  nm. Heating until room temperature and the introduction of air caused the decrease of the 345 nm peak and a little increase of the colloidal absorption band. Considering the long time irradiation necessary to obtain the silver mirror, it is likely that migration of silver atoms and clusters in the PMA matrix is not so easy as in the polysaccharide derivative films.

## 5. CONCLUSIONS

Thin films of CMC<sub>Ag</sub> and CTO<sub>Au</sub> were photolyzed with 253.7 nm light under several reaction conditions. At room temperature in wet air, the irradiated surface of the films finally changed into clear silver or gold mirror. When the CMC<sub>Ag</sub> film was photolyzed at 77 K in vacuum and then heated, 300 nm and 335 nm peaks overlapped with the structureless absorption appeared. These peaks are assigned to certain silver clusters. Although no distinct peaks were noticed in the CTO<sub>Au</sub> film, heating the film until room temperature, followed by the introduction of air brought about the development of colloidal absorption band of gold. These observations are indicative of migration and aggregation of metal atoms and clusters in the film. Considering the control of the aggregation state of photolytic metal by reaction conditions—from cluster to metal film—, metal salts of CMC and CTO are promising starting materials for matrix-supported metal particles.

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