Dyeing of Silk Cloth with Colloidal Gold

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Synopsis

Silk cloth was dyed successfully by dipping it in a gold hydrosol which was prepared in the presence of a cationic surfactant, stearyltrimethylammonium chloride (SC). The color of thus dyed silk cloths is due to colloidal gold particles adsorbed on silk fibers and varies from reddish purple to dark purple according to the periods of dipping time and the amounts of SC in the gold hydrosol used. The mechanism for the adsorption of colloidal gold on the silk fibers is proposed.

INTRODUCTION

Ultrafine metal particles, in general, show a characteristic color due to their plasma oscillation.[1] In particular, ultrafine gold particles dispersed in solid materials show a bright red or purple color which corresponds to absorption of light at about 520 nm. Such phenomenon has long been utilized in coloring of china and glass wares for example, the purple of Cassius, stained glass, ruby glass, and so on.

On the other hand, ultrafine particles of noble metals like gold, platinum, and palladium dispersed in water have been known and called colloidal noble metals.[2] Such dispersion systems, called hydrosols, show a similar color to those dispersed in solid.

As recently reported,[3] noble metal hydrosols can be easily prepared by reducing noble metal salts in aqueous solutions in the presence of surfactants. Colloidal noble metals in the hydrosols tend to be adsorbed on solid materials having a charged surface. For example, colloidal palladium could be adsorbed on cellulose fibers, to be utilized as a catalyst for electroless plating of paper.[4]

We have found that colloidal gold prepared with cationic surfactant was firmly adsorbed on silk fibers to give them reddish purple or dark purple color. In this article, the dyeing procedure of silk using gold hydrosols and mechanism for the adsorption of the colloidal gold in dyeing process are described.

EXPERIMENTAL

Preparation of Gold Hydrosols[3]

Typical preparation procedure is as follows. First, 0.5 mmol of tetrachloroauric acid ($HAuCl_4 \cdot 4H_2O$) was dissolved in distilled water (940 mL). To this solution, a solution (10 mL) of 100 mg of surfactant and a solution (50 mL) of 2 mmol of sodium borohydride ($NaBH_4$) were successively added with vigorous stirring. At that time, colloidal gold particles were formed, resulting in rapid color change and hydrogen generation. After stirring for 10 minutes, a

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gold hydrosol (1 L) having transparent deep red color was obtained. Three different types of gold hydrosols, Au-SC, Au-SD, and Au-PN were prepared using stearyltrimethylammonium chloride (cationic surfactant, SC), sodium dodecylbenzenesulfonate (anionic surfactant, SD), and polyethylene glycol mono-*p*-nonylphenyl ether (nonionic surfactant, PN), respectively.

Dyeing of Cloths

Plain woven standard cloths, which were supplied from Japanese Standards Association and cut into 4 × 4 cm squares, were dipped in a gold hydrosol (100 mL) for a given period of time, washed with water, and air-dried. In some cases, additional surfactant SC was dissolved in Au-SC before use for dyeing.

Characterization of Dyed Cloths

Gold content of dyed cloths was determined by both atomic absorption measurement after dissolving in *aqua regia* and by the reduction of absorbance at 520 nm of a gold hydrosol used. Surfactant SC in Au-SC was analyzed by absorbance at 485 nm of a chloroform solution of extracted ion-pair which was formed from SC and Orange II.[5] Ultrathin slices of dyed silk fibers with colloidal gold on the surface were observed by JEOL Model JEM-1200EX transmission electron microscope at magnifications of 100,000 to 200,000. Visible absorption spectra of gold hydrosols and reflection spectra of dyed cloths were measured with Shimadzu Model UV-240 and Cary Model 17D-1711 spectrophotometers, respectively.

RESULTS AND DISCUSSION

Colloidal Gold (Hydrosols)

Zeta potential of colloidal gold was, as shown in Table I, dependent on surfactant used, positive for Au-SC, negative for Au-SD and Au-PN[3] while these three gold hydrosols showed nearly the same deep red color corresponding to 520 nm absorption as shown in Figure 1.

TABLE I
Some Characteristics of Gold Hydrosols Prepared with Surfactants

Hydrosol	Surfactant	pH	Zeta potential (mV)
Au-SC	Stearyltrimethyl-ammonium chloride	7.00	+23
Au-SD	Sodium dodecyl-benzenesulfonate	4.40	−35
Au-PN	Polyethylene glycol mono-*p*-nonylphenyl ether (n = 10)	3.50	−18

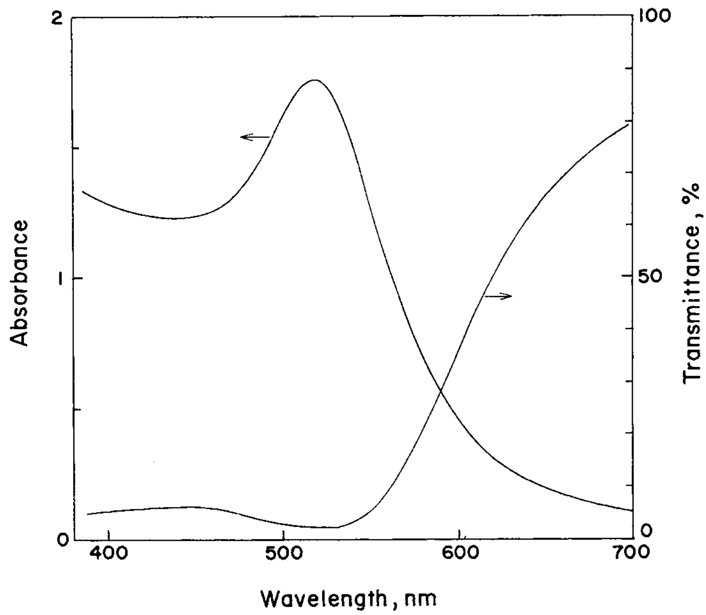

Fig. 1. Absorption spectrum of Au-SC (Au conc. = 98.5 ppm, light path length = 1 cm).

Dyeing of Various Cloths

Typically, eight cloths were tested for dyeing by dipping them in gold hydrosols for 20 h at room temperature. Results are shown in Table II. Silk, wool, and cotton cloths were successfully dyed with Au-SC. In addition, only cotton was dyed with Au-SD. Cloths of regenerated and synthetic fibers were scarcely or not dyed at all with either Au-SC or Au-SD. None of the cloths examined was dyed with Au-PN. Among our specimens, silk cloth was most intensely colored with Au-SC. On the whole, Au-SC having positive colloidal gold is the most suitable for dyeing of natural fibers. In such cases, electro-

TABLE II
Dyeing of Cloths in Gold Hydrosols

Cloth	Hydrosol		
	Au-SC	Au-SD	Au-PN
Silk	+ +	−	−
Wool	+	−	−
Cotton	+	+	−
Viscose rayon	+	−	−
Acetate rayon	−	−	−
Acrylic	±	−	−
Nylon	−	−	−
Polyester	±	±	−

+ + strongly colored, + colored, ± slightly colored, − not colored. Cloths were dipped in gold hydrosols at room temperature for 20 h. Concentration of surfactant in gold hydrosols was 100 ppm.

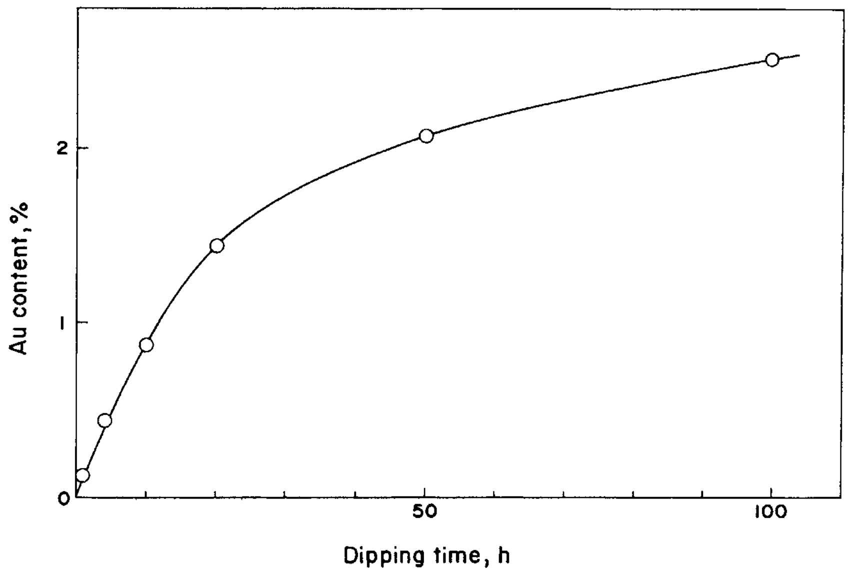

Fig. 2. Relationship between the amounts of gold adsorbed on silk cloth and the periods of dipping time in Au-SC.

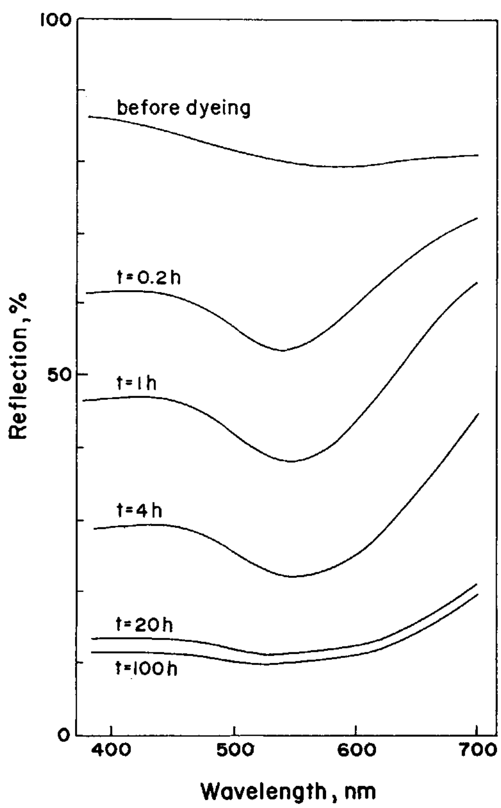

Fig. 3. Reflection spectra of silk cloths dyed with Au-SC (t = dipping time).

static interaction between positively charged colloidal gold particles and negatively charged fibers might be of importance in the dyeing process.

Effect of Dipping Time

The time course of adsorption of colloidal gold on silk cloth was examined by dipping it in Au-SC for varying periods of time. As shown in Figure 2, gold content of the silk cloth gradually increased, but still had not reached a saturated value even after dipping it for 100 h. As colloid adsorption proceeded, color of the silk cloth changed from light purple to deep dark purple. In the reflection spectra of the dyed silk cloths shown in Figure 3, a common dip at 540 nm appears and background refraction gradually decreases as dipping time is prolonged. The dip appearing in these refraction spectra could be attributed to absorption by gold particles on silk fibers as observed in the absorption spectrum of Au-SC shown in Figure 1.

Effect of SC Content in Gold Hydrosols

Dyeing of silk cloth was carried out by dipping it for 20 h in Au-SC hydrosols to which varying amounts of SC had been previously added. As shown in Figure 4, the amounts of gold adsorbed on the silk cloth decrease with increasing concentration of SC in gold hydrosols. In the refraction spectra of cloths thus dyed, shown in Figure 5, a dip appears at 530-540 nm as in those in Figure 3.

The colors of the representative dyed silk cloths are given in Table III. It should be noted that gold contents of silk cloths of No. 2 and No. 4 seems to

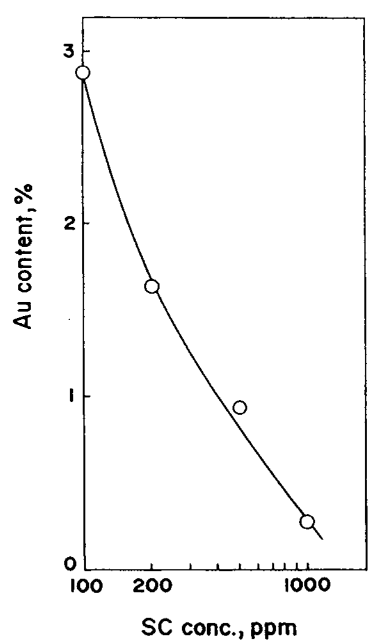

Fig. 4. Relationship between the amounts of gold adsorbed on silk cloths and total SC concentration in gold hydrosols.

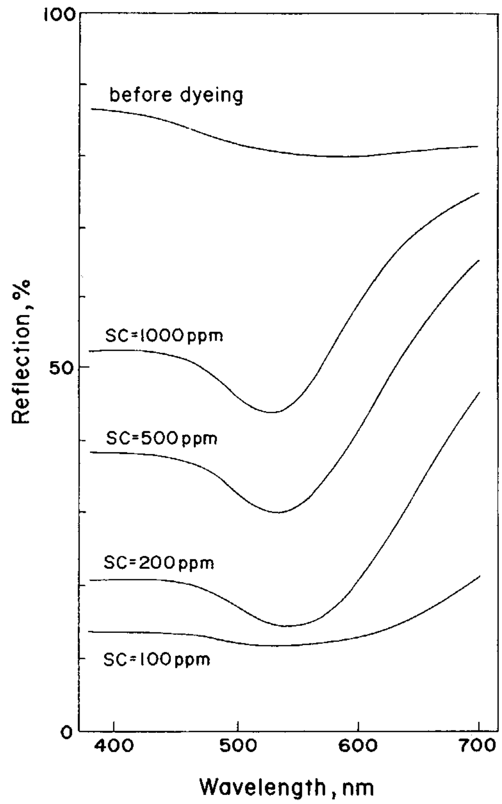

Fig. 5. Reflection spectra of silk cloths dyed by dipping in SC-added Au-SC for 20 h.

be almost equal, while their color tones differ from one another, that is, the former is dark purple and the latter is reddish purple. Transmission electron microscopy (TEM) pictures of the two are shown in Figure 6. This indicates that gold particles on the silk fibers of cloth No. 4 are well dispersed over the entire surface, but particles for No. 2 are located closely in one area and almost absent in the other. It is presumed that, in No. 2 case, adsorption of colloidal gold particles on the fibers proceeded much more rapidly than did their diffusion through the fibers to the inside; therefore, colloid adsorption on the fiber occurred exclusively near the surface of the cloth. Although addition of surfactant SC to the gold hydrosol markedly retarded the colloid adsorp-

TABLE III
Gold Content and Color of Silk Cloths Dyed with Gold Hydrosols

No.	SC conc. in hydrosol (ppm)	Dipping time (h)	Cloth after dyed Gold content (%)	Cloth after dyed Color
1	100	0.2	0.03	Light purple
2	100	4	0.47	Dark purple
3	100	20	1.33	Blackish purple
4	500	20	0.50	Reddish purple
5	1000	20	0.18	Light reddish purple

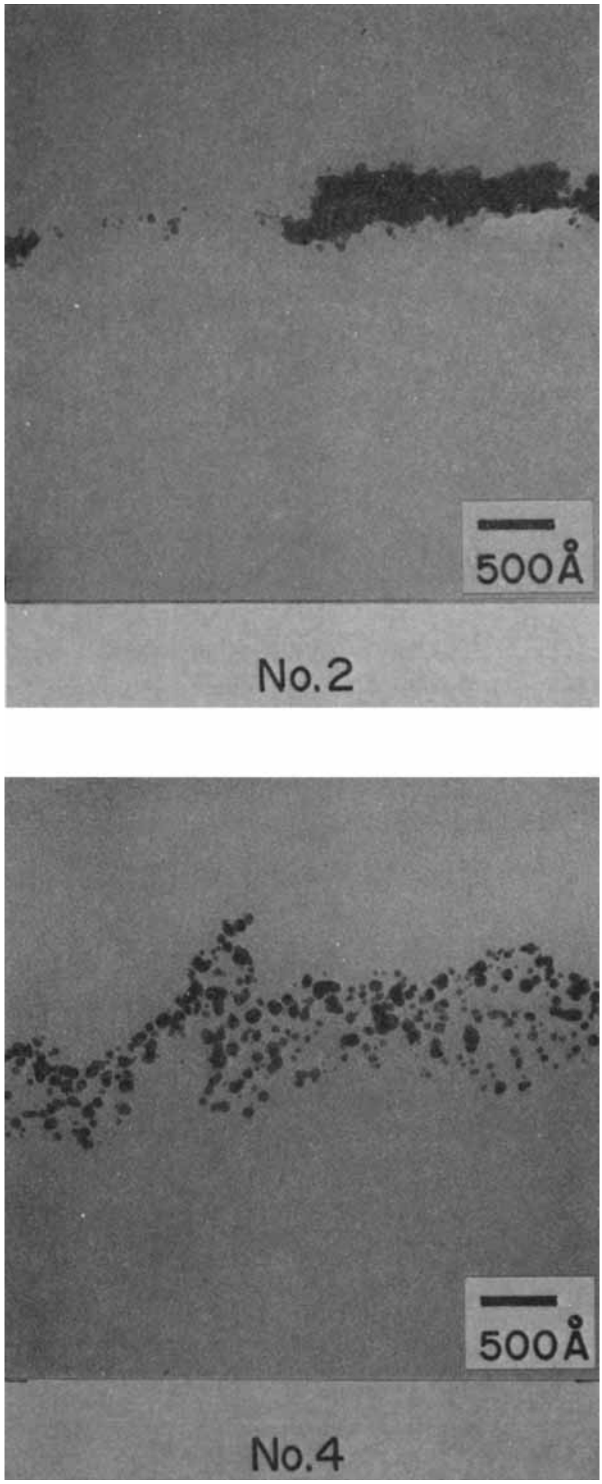

Fig. 6. Transmission electron micrographs of the slices of silk fibers dyed with gold hydrosols (numbers of cloth correspond to those in Table III).

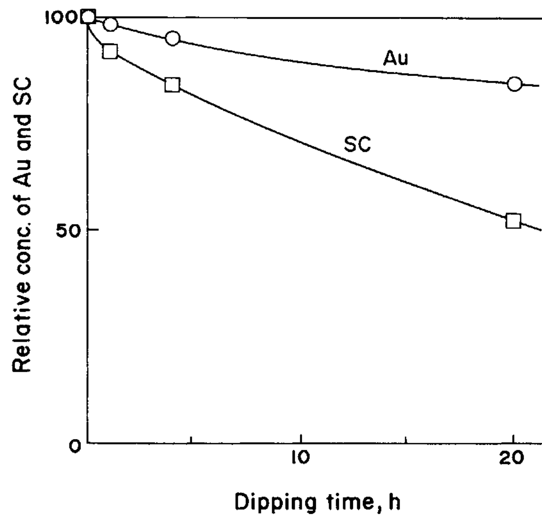

Fig. 7. Time-course of the relative concentrations of gold (○) and SC (□) in Au-SC (initial = 100) during dyeing of silk cloth.

tion, additional electrolyte NaCl had only a slight effect on adsorption rates up to a concentration of 100 mM. Agitation or enhancement of temperature resulted not only in accelerated colloid adsorption to a certain extent, but also in uneven dyeing.

Mechanism for Colloidal Gold Adsorption

As stated above, surfactant SC contained in Au-SC is considered to play an important role in the dyeing process.

To confirm this, the concentration of SC in Au-SC was determined during the course of dyeing of silk cloth as well as that of gold. The results are given in Figure 7, indicating that the concentration of SC decreases more rapidly than does that of gold. It implies that the silk fibers adsorb SC prior to colloidal gold.

Next, the effect of pretreatment of silk cloth with SC was examined. As a result, it was found that silk cloth previously dipped in 100 ppm solution of SC for 20 h could not be dyed in Au-SC, while that dipped for 1 h was smoothly dyed in Au-SC. These data indicate that surfactant SC is adsorbed slowly on silk fibers and that SC thus adsorbed hinders colloidal gold adsorption on the fibers. Such hindrance by adsorbed SC might cause the above-mentioned retardation of dyeing in SC-added Au-SC. On the other hand, when SC in Au-SC was removed by dialysis, colloidal gold particles aggregated to form black precipitates.

These results lead to the following mechanism for the adsorption of colloidal gold on silk fibers, as illustrated in Figure 8. At first, free SC molecules located near the silk fibers are adsorbed on the surface of the fibers. Then, other SC molecules adsorbed on colloidal gold particles near the fibers are desorbed. The colloidal particles thus unstabilized are adsorbed on the nearest surface of the fibers.

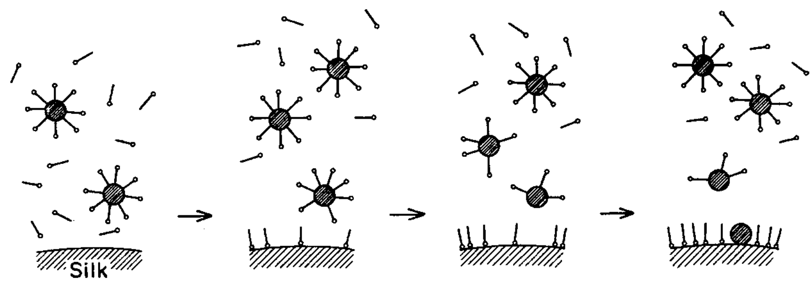

Fig. 8. Proposed mechanism for the adsorption of colloidal gold on silk fibers. (⊘) Au particle; (—o) SC molecule.

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