Highly Concentrated Pastes of Nano-Sized Metal Particles for Ink Jet Printing

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Abstract

Preparation and utilization of nano-sized metal particles are of interest in a variety of fields including electronics, optics, catalysts and colorants. In order to utilize the nano-sized particles industrially, mass production of stable and highly concentrated dispersion is necessary. We have developed a novel method to produce such dispersions of nano-sized metal particles having 2 – 50 nm diameter. The method consists of colloidal stabilization by specially designed block copolymer and reduction of metal ions under presence of alkanol amine.

Up to now we have succeeded to prepare the colloidal pastes of Ag, Au, Pt, Pd, Ni, Bi and Au/Ag alloy with metal concentrations of more than 30% in a variety of solvents such as water, alcohols, esters, ketones and aromatic hydrocarbons.

These colloidal pastes are applicable to Ink Jet Printing owing to their excellent stability and nano-sized diameter. Printed patterns exhibits metal like appearance, electro-conductivity, clear red and yellow colors and catalytic activity depending on species and concentration of the metal.

Introduction

We have already developed a novel method to prepare the highly concentrated and stable dispersions of gold and silver nano-particles having diameter of 5 - 15 nm.[1] The method consists of two key technologies. The first one is protection of particles from their mutual coagulation using a special kind of comb-shaped block copolymer. The second one is reduction method of the metal ions. We found some alkanol amines reduce noble metal ions and yield nano-particles at industrially controllable rate.

Schematic illustration of the nano-sized gold particles stabilized by the comb-shaped block copolymer is shown in figure 1. The polymer has multiple amino groups on the main chain. The side chains with varying chemical structure and polarity are available. Choice of the side chain enables the polymer to dissolve in various kinds of solvents.

Besides gold and silver, we applied the above mentioned method to obtain the pastes of platinum, palladium, nickel, bismuth and Au/Ag alloy in this work. Characteristics of obtained pastes and the utilization of the pastes including Ink Jet Printing will be reported.

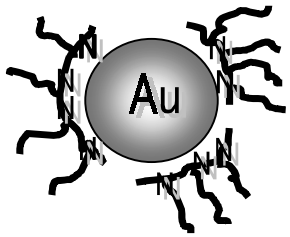

Figure 1. Schematic Illustration of gold nano-particle stabilized by comb-shaped block copolymer

Pastes of Nano-Sized Metal Particles

Using the comb-shaped block copolymer as stabilizer and an alkanol amine as reducing aids, nano-particle pastes listed in Table 1 were prepared. These pastes show no settling and no coagulation after 1 month's storage at room temperature. Moreover, even if the solvent in the pastes evaporates and pastes are dried, the pastes easily dissolves again in the solvent. This kind of stability will be suitable for Ink Jet Printing.

Table 1. Characteristics of Nano-Sized Metal Pastes

Metal	Au	Ag	Pt	Pd	Ni	Bi	Au / Ag
Particle Size (nm)	15 - 45	10 - 75	1 - 3	5	30 - 40	20 - 30	20 - 30
Solvents*1	W, A, S	W, A, S	W, A	S	S	W, S	W, A
Max. Metal conc (%) *2	30	30	5	5	5	5	5
Max. Metal /Solid *3	90	96	50	40	50	70	90

*1; W; Water, A; Alcohol, S; Organic solvents other than alcohol

*2; Maximum metal concentration in pastes

*3; Maximum weight ratio of Metal / (Metal + Polymer)

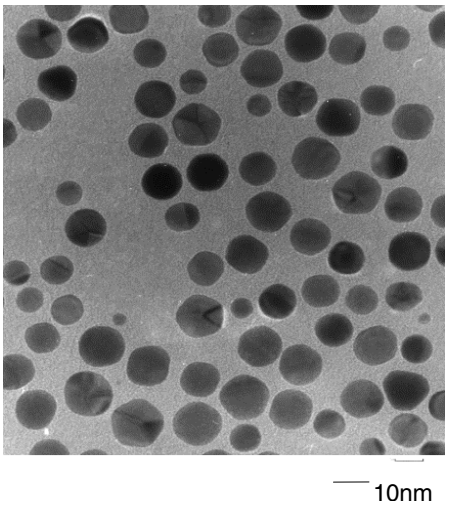

Figure 2. TEM photograph of gold nano-particle

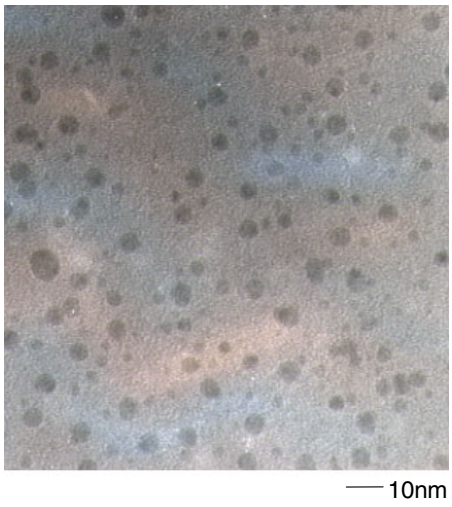

Figure 3. TEM photograph of silver nano-particle

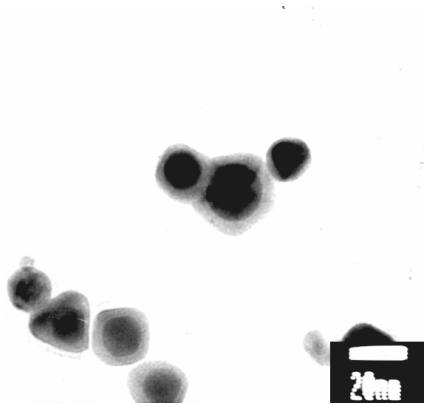

Figure 4. TEM photograph of gold-core / silver-shell alloy nano-particle (Au/Ag=1/2 by weight)

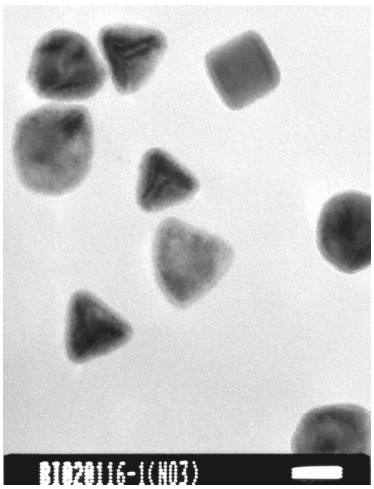

Figure 5. TEM photograph of bismuth nano-particle

In figures 2, 3, 4, and 5, TEM photographs of gold, silver, gold-core/silver-shell alloy and bismuth nano-particles are shown, respectively. These photographs are typical ones and photographs of all nano-particles listed in Table 1 will be presented in the conference.

Plasmon Light Absorption by Gold and Silver Nano-Particles

Free electron within a nano-sized metal particle is resonant with the light of specific wave length and the particle absorbs the light. For instance, a gold particle (ca 15 nm) absorbs light of ca 525 nm and its dispersion exhibits red color. This mechanism is called plasmon light adsorption. Typical light absorbance spectra for suspension of silver and gold nano-particles are shown in Figure 6. Relatively sharp absorption peaks are observed in both silver and gold.

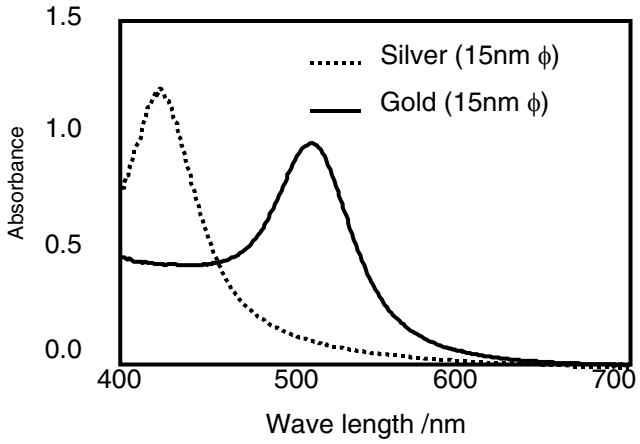

Figure 6. Light absorption spectra for suspensions of silver and gold nano-particles.

Coloring characteristics of plasmon light absorption by silver nano-particle are compared to that of conventional organic pigment. As silver nano-particle shows yellow color, Pigment Yellow 110 (PY110), with highly weather fastness and clear yellow color, was used as the reference pigment.

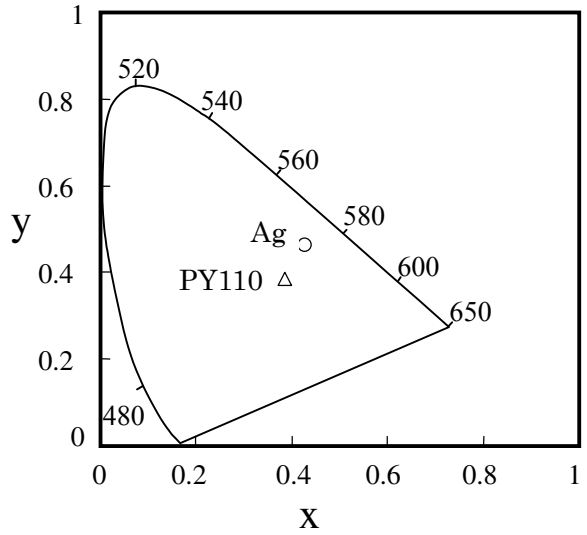

Figure 7. Comparison of color saturation between silver nano-particle and Pigment Yellow 110

In figure 7, positions of the color by silver nano-particle and by PY110 at the same Y value are shown on the CIE coordinates. Coloring by silver nano-particle was clearer than PY110. Moreover, color strength per unit weight of silver nano-particle was found to be 10 times higher than PY110.

Plasmon light absorption depends not only on the metal species but on the particle size. We succeeded to control the particle size of gold nano-particle within 15 – 45 nm.[2] As the particle size increased, the wavelength at the light absorption maximum (λmax) increased and the suspension exhibited more bluish color. (See figure 8.)

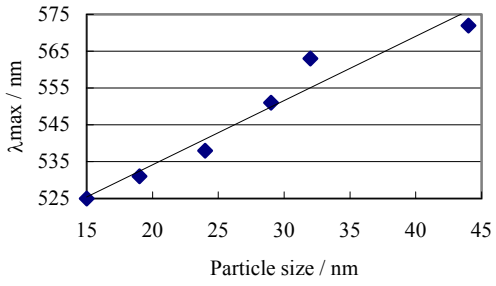

Figure 8. Relation between particle size of gold and wavelength at absorption maximum (λmax)

Gold-core / silver-shell nano-particle showed wide plasmon absorption band between 400 – 500 nm as shown in Figure 9. This type of absorption spectrum cannot be obtained by a simple mixture of gold and silver nano-particles.

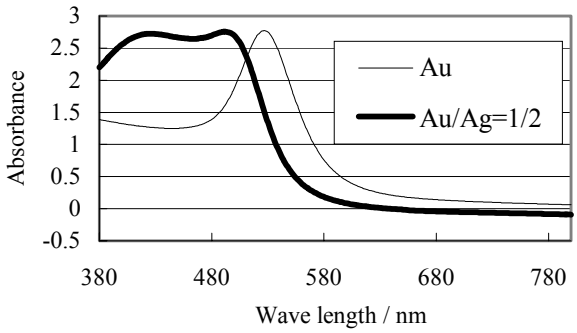

Figure 9. Plasmon light absorption spectra of gold-core / silver-shell nano-particle suspension.

Of course gold and silver are noble metals and excellent weather, heat and light stability can be expected. Gold, silver and their alloy nano-particles could be used as novel colorants or optical materials possessing above mentioned optical properties. Application of these metal pastes to Ink Jet Printing would lead to creation of new technology fields.

Thin Metal Film Preparation

The metal contents in solid components in Table 1 are high enough to yield a thin film with a metal like appearance by a simple coating & drying process. A silver paste (Ag conc.; 30%, Ag cont. in solid; 95%, solvent; Ethanol) was diluted by ethanol, spin-coated on the glass plate and dried at room temperature. A thin film with metal like appearance as shown in figure 10 was obtained. This film, however, didn't show electro-conductivity.

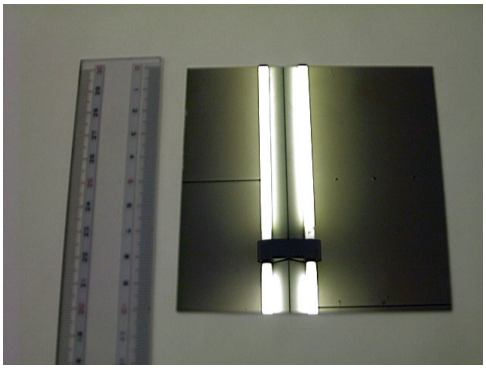

Figure 10. A thin film with metal like appearance using silver nano-particle paste

The film began to exhibit electro-conductivity by heating. A paste with higher metal contents in the solid component showed conductivity at lower temperature. (See figure 11.) Films containing 96% of silver nano-particle exhibited surface electro resistance less than 10 Ω/sq at 120 – 150°C. In figure 12, electro-conductivity of films containing 96% of silver nano-particle is shown as functions of the baking time. The conductivity appeared within 10 minutes both at 120°C and 150°C. These observation leads to a possibility that plastics such as PET could be used as substrates.

The polymer contained in the film cannot be considered to degrade by heating at 120°C – 150°C for less than 10 minutes. Possible mechanism for the conductivity will be discussed.

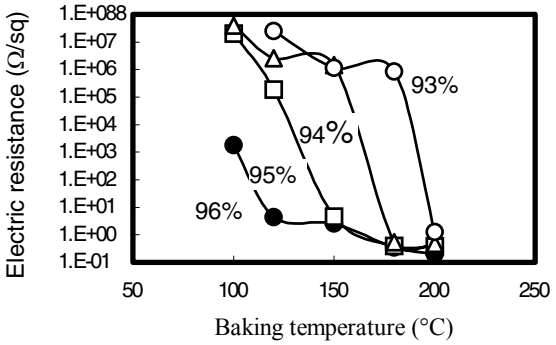

Figure 11. Surface electro-resistance of films containing silver nano-particle as functions of baking temperature at different silver contents

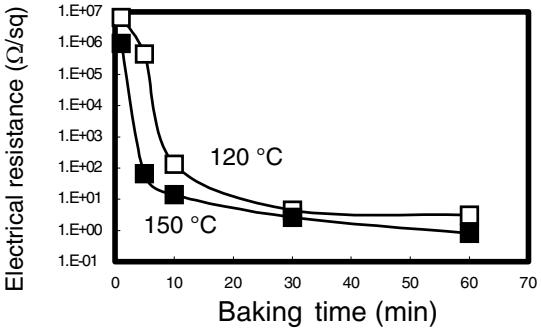

Figure 12. Electro-conductivity of films containing 96% of silver nano-particles as functions of baking time

Figure 13 is a typical output pattern by Ink Jet Printing using silver nano-particle containing ink. Since the stability of the silver paste is excellent, the ink is applicable to both the thermal and pieszo type printers.

As for the detail of Ink Jet Printing application and drawing electronic circuit pattern, please listen to another presentation at NIP19. (T. Oguchi, "Formation of precise electrically conductive pattern using metal colloid I-J ink)

Figure 13. Typical output pattern by Ink Jet Printing using silver nano-particle containing ink (by courtesy of Morimura Chem. Co., Ltd.)

Conclusion

Highly concentrated pastes of nano-sized metal particles were developed. These pastes possess unique optical and electrical properties. The pastes also possess enough stability for applying to Ink Jet Printing Technology.

References

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2. A. Ono, T. Nanke, H. Ishibashi, T. Terada, T. Kobayashi, Congress book, 55th Colloid and Interface Chem., p.78 (2002)

Biography

Toshikatsu Kobayashi received his B.S. degree in Engineering from the Kyoto University in 1978 and a D. Eng. from Kyoto University in 1993. Since 1980 he has worked for Nippon Paint Co., Ltd., Neyagawa, Japan. His work has primarily focused on the preparation and stabilization of particle dispersed system. He is chairman of editorial committee of J. Jap. Soc. Colour Material.