Laser Printing of Translucent Plasmonic Multicolor Images Based on Gold Nanoparticles

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ABSTRACT

Gold nanoparticle ensembles were prepared by laser dewetting from a gold thin film on a glass substrate. The gold film was scanned by infrared laser (1064 nm) using a fiber laser scanner. The morphology, color, and shading of the nanoparticles were controlled by changing two parameters, the laser intensity and the laser scan rate. Laser printing of a multicolor image was successfully demonstrated. This simple method would be applied to patterning of electrodes and semiconductor films with gold nanoparticle ensembles with different optical properties.

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Keywords : Localized Surface Plasmon Resonance, Gold Nanoparticle Ensemble, Near Infrared Laser Printing, Laser Dewetting

1. Introduction

Plasmonic metal nanoparticles are used as photonic materials because of their strong light absorption and unique optical properties.¹ We found plasmon-induced charge separation (PICS)^{2,3} at the interface between plasmonic metal nanoparticles and semiconductor and applied it to wide variety of photoelectrochemical devices including photocatalysts,² photovoltaics,^{2,4} photochromic displays and memories,^{5,6} and photofabricated nanomaterials.^{7,8} Electrochromic displays are additional electrochemical applications of plasmonic nanomaterials.^{9–12} For preparation of those plasmonic devices, it is often necessary to immobilize plasmonic nanoparticles onto solid substrates. In addition, it is useful if the solid surface can be patterned with metal nanoparticles with different optical properties, since the patterning allows us to develop arrays of plasmonic photodetectors and chemical sensors, and to design photocatalytic windows and translucent solar cells that look like “stained glasses” for decorative purposes.

A laser dewetting^{13,14} and ablation^{15–17} method gives a convenient way to pattern plasmonic surfaces.^{15–20} A solid surface is coated with a metal thin film by evaporation or sputtering, and the film is scanned with a laser beam for thermal nanoparticulation and ablation of the metal. However, it usually requires expensive high-power fast-pulse lasers. We recently developed a more convenient

and less expensive laser dewetting method for plasmonic patterning and drawing with silver nanoparticles using an infrared fiber laser scanner.²¹ This class of laser scanners are known and commercially available also as laser markers for marking of plastic bottles, glassware, and so on. However, if silver nanoparticles are in contact with a semiconductor such as TiO₂, the nanoparticles are oxidized under illumination to silver ions because of PICS.^{5,22} Although the photoinduced oxidation can be exploited for multicolor photochromism^{5,23} and nanophotonic etching,²⁴ silver nanoparticles are not suitable for long-term use of photocatalysts and wet-type photovoltaic cells. Gold nanoparticles are therefore used instead of silver in particular for those long-term applications.³ Because of higher Tammann temperature²⁵ and melting point, the morphology control of gold nanoparticles could be more difficult than that of silver nanoparticles. In addition, gold has the longer plasma wavelength and gold nanoparticles tend to show reddish colors. It is therefore much more difficult for gold nanoparticles to exhibit multi-colors in comparison with silver nanoparticles.^{26,27} In the present work, we studied on laser dewetting and ablation of gold films (Fig. 1) and achieved multi-color laser printing with plasmonic gold nanoparticles by using the cost-effective infrared fiber laser scanner.

2. Experimental

A thin gold film (10 nm thick) was formed by ion sputtering

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Figure 1. Schematic illustration for the laser printing with plasmonic gold nanoparticles.

Figure 2. Transmitted colors of the gold nanoparticles on a glass substrate. Laser intensity was (a) 0; (b) 42; (c) 85; (d) 170; (e) 212; (f) 297 J cm⁻². Laser scan rate was 100 mm s⁻¹. The frame and grids were not scanned with laser as was the area for (a).

Figure 3. Transmission spectra of the gold nanoparticles on a glass plate. Laser intensity was 0–297 J cm⁻². Laser scan rate was 100 mm s⁻¹.

(E-1030, Hitachi High-Technologies) on a glass substrate (1.1 mm thick). The gold film was scanned with a near-infrared laser beam (wavelength = 1064 nm; intensity = 42–297 J cm⁻²; beam diameter ~10 μm; laser pulse frequency = 60 kHz; pulse width = 100 ns; laser scan rate = 10–500 mm s⁻¹) using a fiber laser scanner (YS-P20-SP, Sun Instruments). Optical properties of the prepared samples were investigated by using an ultraviolet-visible-near-infrared spectrophotometer V670 (JASCO), and morphologies and distributions of the nanoparticles were observed using a scanning electron microscope (SEM) JSM-7500FA (JEOL).

3. Results and Discussion

The Au film (10 nm thick) before laser scanning exhibits a greenish color as shown in Fig. 2a. Its transmittance spectrum is shown in Fig. 3. The transmittance in a short wavelength range (<550 nm) was low because of light absorption based on interband transition from d-band to sp-band of gold. The low transmittance in a long wavelength range (>550 nm) is due to light reflection since the interconnected small gold nanoparticles (~10 nm) constitute a thin metallic layer as the SEM image in Fig. 4a shows. As a result of those absorption and reflection, the gold film has the transmittance peak at ~550 nm and looks green.

The gold film on a glass plate was scanned by the infrared laser, and changes in the color, transmittance spectrum, and the surface morphology of the samples were examined. The laser scan rate was 100 mm s⁻¹, the pulse frequency was 60 kHz, and the laser intensity per pulse was changed in the range of 42–297 J cm⁻². As shown in Figs. 2b–2f, transmitted color of gold nanoparticles on a glass substrate was white at 42 J cm⁻², and the color changed to more reddish ones with increasing laser intensity to 170 J cm⁻², and gradually bleached as the intensity was increased further to 297 J cm⁻².

The transmittance spectra of the laser-scanned samples are shown in Fig. 3. A dip was observed at 520–550 nm in each spectrum. As

the laser intensity was increased from 42 to 170–212 J cm⁻², the dip became deeper. The transmittance in the >800 nm wavelength range was increased as the laser intensity was raised. These spectral changes are responsible for the reddening behavior. At intensities higher than 212 J cm⁻², the dip became shallower, corresponding to the bleaching.

Those spectral changes should stem from morphological changes of the gold nanoparticles. We therefore observed the sample surface by using SEM (Figs. 4b–4f). The average particle size and the number of particles per 1 μm² are listed in Table 1. As the laser intensity was increased, the particle size decreased and became more uniform, and the particle density increased basically.

The tendencies of these morphology changes are similar to those observed for laser dewetting of silver.²¹ When the laser intensity was low, the gold thin film transformed into a small number of large, polydisperse particles. As the laser intensity was increased, the particles were further divided into many smaller particles, for decreasing the area of the gold-glass interface with high interfacial energy. Resonance wavelength of plasmonic metal nanoparticles approach the plasma wavelength as the particle size decreases. Therefore, as seen in Fig. 3, the transmittance in the 500–600 nm range decreased and that in the longer wavelength range increased as the intensity was increased from 0 to 170–212 J cm⁻². As a result, the color of the sample became more reddish, even though surface oxides and roughness might also affect the colors.

However, at higher intensities, the transmittance dip became shallower because the melted nanoparticles became more spherical and gold partially evaporated due to laser ablation. It should be noted that the absorption of spherical gold nanoparticles is roughly proportional to the particle volume.²⁸ At the same laser intensity, the average particle size of the resultant gold nanoparticles was slightly larger than that of the silver nanoparticles.²¹ This stems mainly from higher Tammann temperature,²⁵ melting point, and surface tension²⁹

Figure 4. SEM images of gold nanoparticles on a glass plate obtained by laser scan at (a) 0, (b) 42, (c) 85, (d) 170, (e) 212, and (f) 297 J cm⁻². Laser scan rate was 100 mm s⁻¹.

Table 1. Average particle size and particle density of Au NPs prepared at different laser intensity.

Laser intensity/J cm ⁻²	42	85	170	212	297
Average particle size/nm	119.2 ± 78.5	25.15 ± 18.3	21.25 ± 8.68	25.51 ± 7.65	9.25 ± 3.03
(Number of particles counted)	(42)	(150)	(167)	(404)	(343)
Particle density	5.01	1.42 × 10 ²	1.11 × 10 ²	2.15 × 10 ²	3.69 × 10 ³

Table 2. Tammann temperature,¹⁶ melting point, boiling point, surface tension,²⁹ and work of adhesion²⁹ of gold and silver.

Metal	Tammann temperature /°C	Melting point /°C	Boiling point /°C	Surface tension /N m ⁻¹	Work of adhesion /mN
Au	395	1064	2856	1.1 (at 1070 °C)	246
Ag	344	962	2162	0.8 (at 970 °C)	174

of gold. Table 2 lists those values together with boiling point and work of adhesion.²⁹

Next, the scan rate was changed to 10 and 500 mm s⁻¹. Laser intensity was 212 J cm⁻². As shown in Figs. 5a–5c, the transmitted color of the samples became paler with increasing scan rate. Color of the sample before laser scanning is also shown for comparison (Fig. 5d). The transmittance dip at 520–550 nm became shallower (Fig. 5e), as expected from the color changes. This behavior can be explained simply in terms of decreasing laser exposure time.

From these results, it is concluded that multicolor drawing with plasmonic gold is possible by tuning the laser intensity and scan rate. On the basis of these results, we drew a multicolor image on a 4 × 3 cm glass substrate by changing the laser intensity and scan rate during laser scanning (Fig. 6). It is obvious that the multicolor image was successfully drawn by the simple method.

4. Conclusions

Gold nanoparticle ensembles were prepared by laser dewetting from a gold thin film on a glass substrate. The color and shading of the substrate can be controlled by changing two parameters, the laser

Figure 5. (a–d) Transmitted colors and (e) transmission spectra of the gold nanoparticles on a glass substrate. Laser scan rate was (a) 10; (b) 100; (c) 500 mm s⁻¹. Laser intensity was (a–c, e) 212; (d) 0 J cm⁻².

intensity and the laser scan rate. Laser printing of a multicolor image was successfully demonstrated. This method is expected to be used for preparation of patterned gold nanoparticle ensembles on transparent electrodes and semiconductors, so that the ensembles would be applied to well-designed and decorative photocatalysts and photovoltaic devices that look like stained glasses, besides optical materials.

Figure 6. Laser-printed multicolor image of tulip drawn on a 4×3 cm glass plate.

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