

# Heat-generating property of a local plasmon resonator under illumination

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We have investigated the heat generation from gold nanoparticles resulting from their local plasma resonance. We have demonstrated the self-assembly of Au nanoparticle arrays/dielectric layer/Ag mirror sandwiches, i.e., a local plasmon resonator, using a dynamic oblique deposition technique. The thicknesses of the Au and dielectric layers were changed combinatorially on a single substrate. As a result, local plasmon resonator chips were successfully fabricated. Because of strong interference, their optical absorption can be controlled between 0.0% and 97% in the near-IR region, depending on the thickness of the dielectric layer. We evaluated the heat generation from Au nanoparticles by measuring the temperature of water with which a cell prepared on a chip is filled under laser illumination. The change in the water temperature is proportional to the optical absorption of the local plasmon resonator chips. This suggests that the photothermal conversion efficiency can be controlled by interference. These features make the application of the local plasmon resonator to nanoheaters, which can spatiotemporally control heat generation, suitable. © 2011 Optical Society of America

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Au nanoparticles absorb electromagnetic radiation strongly around their plasma resonant frequency, and their generation of heat under illumination has been investigated in the field of thermoplasmonics [1,2]. They have been attracting considerable attention because of their fast response, flexibility in terms of heating area choice, and no requirement for electrical connection between nanoparticles. These unique photothermal properties of Au nanoparticles are ideal for a number of applications, such as microfluidics [3,4] and photoacoustic applications [5]. However, two-dimensional Au nanoparticle heaters, which are often fabricated by electron-beam lithography of Au thin films on a glass or Si substrate, absorb only a few tens of percent of the incident light even at the wavelength of the local plasma resonance [6,7]. Therefore, they are ineffective from the viewpoints of not only fabrication cost but also photothermal conversion efficiency. In addition, it is difficult to spatially control the heat generation because photothermal conversion efficiency on a uniform nanoparticle array is independent of the illuminated position.

Recently, we demonstrated the self-assembly of Au nanoparticle arrays/dielectric layer/Ag mirror sandwiches, i.e., the local plasmon resonator, by using a dynamic oblique deposition (DOD) technique [8]. The dielectric layer consists of two layers. One layer controls the shape of the Au nanoparticles and is named the “shape control layer” (SCL). The other layer controls the optical path length and is named the “phase control layer” (PCL). The local plasmon resonators exhibit resonance absorption in the near-IR region and excellent surface-enhanced Raman scattering properties. It has been reported that the optical absorption of the local plasmon resonator can be controlled between 0% and ~99.9% by varying the thickness of the dielectric layer.

Although the absorption may be controlled by a single layer pigmented by dye molecules, it is not easy to reduce the Fresnel reflection. The conditions of the nearly perfect reflector and absorber can be achieved easily by using both interference and a very thin layer with high

extinction coefficient, such as Au nanoparticle arrays [9]. In addition, Au is more stable thermally and chemically than the dye molecules. If it is possible to transfer the heat in a controlled manner to the surrounding medium from the Au nanoparticle array, we will be able to develop unique highly efficient heaters that can spatiotemporally control the heating area. In this study, we show that the photothermal conversion efficiency can be widely controlled by changing the optical path length in local plasmon resonators.

Figure 1(a) indicates schematically the layered structure of a chip of the local plasmon resonator. To obtain chips with various photothermal conversion efficiencies, we prepared the local plasmon resonators with different thicknesses of PCLs on a single substrate of 50 mm × 50 mm by DOD. The preparation method of the local plasmon resonator chips is basically the same as that reported in our previous paper [8]. First, a smooth Ag layer of 200 nm thickness was deposited on a glass substrate. On this Ag mirror surface, a PCL of SiO<sub>2</sub> of 0–220 nm thickness was deposited from the normal direction to the surface. A series of different SiO<sub>2</sub> thicknesses were realized on a single substrate by moving a shutter incrementally across the sample during SiO<sub>2</sub> deposition. On the PCL, a SCL of SiO<sub>2</sub> was prepared that was up to 400 nm thick. The preparation process of the SCL was slightly modified in this study. During the deposition of the SCL, the deposition angle measured from the surface normal was fixed at 80°, and the substrate was rotated continuously and rapidly. As the result, surface morphology of the SCL became isotropic. An Au nanoparticle layer of 8.6 nm thickness was deposited at a deposition angle of 83.4° onto the SCL. In this way, we prepared local plasmon resonator chips with various thicknesses of PCL. No significant in-plane optical anisotropy was observed.

Optical reflection measurements on every chip were carried out using a single-beam spectrophotometer in the wavelength range of 300 nm <  $\lambda$  < 1700 nm. To evaluate heat generation from the chips under illumination,

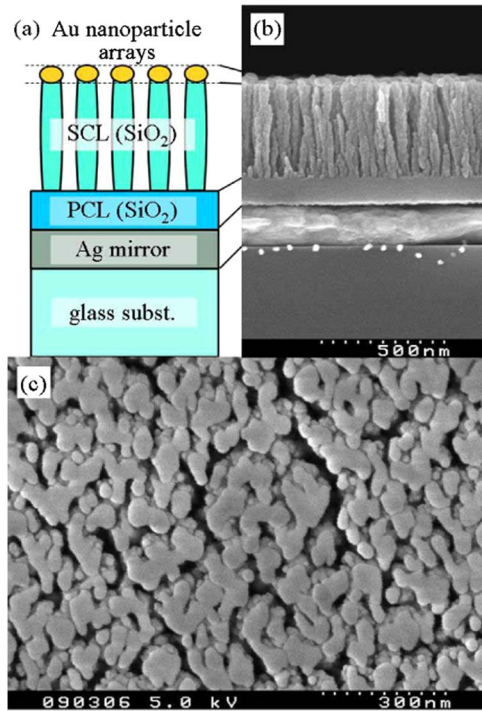


Fig. 1. (Color online) (a) Schematic drawing of the side view and SEM images of (b) cross section and (c) surface morphology of the local plasmon resonator that has the Au nanoparticle arrays/SCL/PCL/Ag mirror structure.

we immersed the chips in water and measured the temperature increase of the water. We created a cell (6 mm diameter with a 0.5-mm-thick silicone rubber spacer) on the chip and filled the cell with  $14 \mu\text{l}$  of water. After the irradiation of the semiconductor laser ( $\lambda = 785 \text{ nm}$ ) on the local plasmon resonator chip was started, we measured the temperature increase of the water using a thermal viewer (CPA2003, CHINO) until the temperature reached equilibrium.

Figures 1(b) and 1(c) show typical scanning electron microscope (SEM) images of the cross section and surface morphology, respectively, of the prepared local plasmon resonator chip. The multilayered structures of Au nanoparticle arrays/SCL/PCL/Ag mirror are realized by DOD, as depicted schematically in Fig. 1(a).

Figure 2 depicts the selected absorption spectra of the local plasmon resonator chips, whose PCL thicknesses,  $h_{\text{PCL}}$ , are 80 and 220 nm. It should be noted that both chips have exactly the same structure except for the thickness of the PCL. Nevertheless, the spectra are very different. The optical absorption of the local plasmon resonator changes between  $\sim 0.0\%$  and  $97\%$  at different photon energies, depending on  $h_{\text{PCL}}$ . For example, it is remarkable that the optical absorption on  $h_{\text{PCL}} = 80 \text{ nm}$  becomes greater than  $95\%$  at a photon energy of around  $1.6 \text{ eV}$ , whereas that on  $h_{\text{PCL}} = 220 \text{ nm}$  becomes approximately  $0\%$  at a similar photon energy. On the other hand, at a photon energy of around  $2.1 \text{ eV}$ , the optical absorption on  $h_{\text{PCL}} = 220 \text{ nm}$  becomes greater than  $95\%$ , whereas that on  $h_{\text{PCL}} = 80 \text{ nm}$  becomes less than  $5\%$  at a similar photon energy. Consequently, the coupling of the light to the local plasmons in Au nanoparticles was successfully modified by interference.

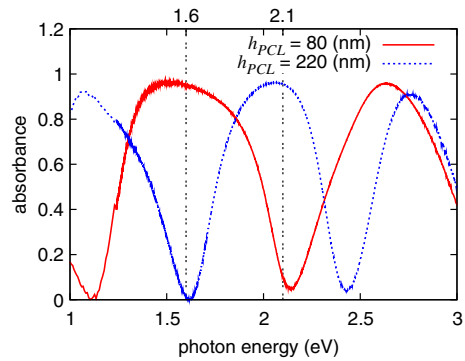


Fig. 2. (Color online) Spectrum comparison of local plasmon resonator chips whose PCL thicknesses are  $h_{\text{PCL}} = 80$  and  $220 \text{ nm}$ .

Figure 3(a) depicts the typical results of the evaluation of the photothermal conversion, where the temperature increase of the water in the cell created on the local plasmon resonator chip was measured as a function of the irradiation time of the laser. The temperature of the water in the cell begins to increase immediately after the laser irradiation; it reaches equilibrium temperature at an irradiation time longer than  $10 \text{ s}$ . The equilibrium temperature of the water on the chip with high optical absorption is much higher than that with low absorption. In contrast, the time constant of the temperature increase of the water appears independent of the optical absorption of the chips.

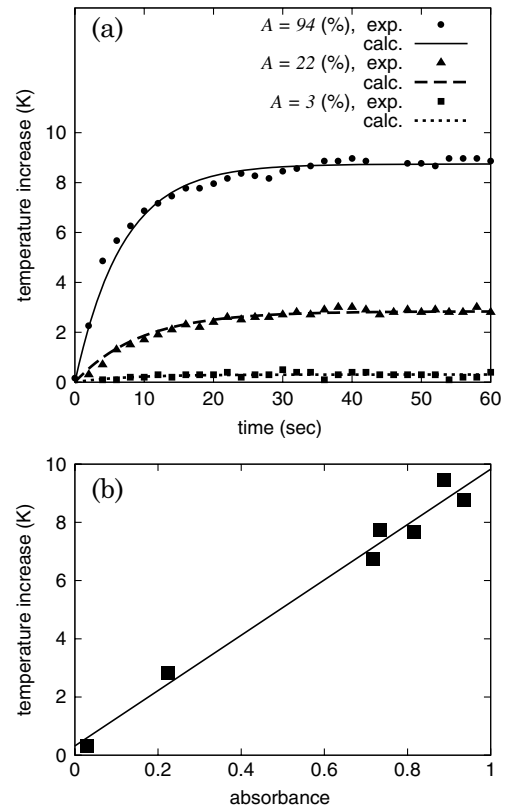


Fig. 3. Photothermal properties of local plasmon resonators. (a) Trace of the temperature increase of the water in the cell. Both measured and calculated (solid curves) distributions are shown. (b) The temperature increase of the water in the cell at equilibrium as a function of the optical absorbance. The solid line represents a linear fit, where  $Q = 8.4 (\text{mW/K})$ .

We discuss the photothermal response of local plasmon resonator chips based on a simple model. We assumed that all of the photon energy absorbed by the Au nanoparticles is converted to heat energy and is immediately transferred to the water in the cell. In addition, the energy flowing out of the water in the cell is assumed to be proportional to the difference of the temperature between the water,  $T$ , and the surroundings (air and the wall),  $T_0$ . These assumptions allow us to write the rate equation for the temperature of the water in the cell at time  $t$  as follows:

$$\frac{dT}{dt} = \frac{1}{CM}(AI - Q(T - T_0)). \quad (1)$$

In this equation  $C$ ,  $M$ ,  $A$ , and  $I$  are the specific heat capacity, mass of the water, optical absorption of the chip, and intensity of the laser, respectively. Thus, the temperature increase of the water in the cell,  $T - T_0$ , is given by

$$T - T_0 = \frac{AI}{Q} \left(1 - e^{-\frac{Q}{CM}t}\right), \quad (2)$$

where  $T = T_0$  at  $t = 0$ . In the present experiments,  $I = 80$  mW and  $M = 0.014$  g. According to the literature, the value of  $C$  is  $4.2$  J/(gK). The optical absorption  $A$  is measured on each chip immersed in the water at the wavelength of  $785$  nm. The lines shown in Fig. 3(a) are the results of fitting Eq. (2) with the experimental data, where only  $Q$  is a fitting parameter. Remarkably, the calculation agrees well with the measurements. If a significant amount of the heat generated in Au nanoparticles escapes to the ambient medium and is not transferred to the water in the cell, the fitting would become poor. The temperature increase of the water in the cell tends to saturate after  $\sim 10$  s of laser irradiation. Figure 3(b) shows the equilibrium temperature increase of the water,  $(T - T_0)|_{t \rightarrow \infty}$ , as a function of the optical absorption  $A$  of the chips. Clearly the temperature increase is proportional to the optical absorption and it is consistent with Eq. (2). Consequently, the photon energy absorbed into the Au nanoparticles is converted into heat and transferred to the surrounding water efficiently. In addition, we demonstrated that heat generation from the local plasmon resonator can be controlled by tuning the coupling of light to the local plasmons in Au nanoparticles by changing the thickness of the PCL.

In this study, we used cells that are much larger than the common microchannels for microelectromechanical

system devices. This large cell size limits the maximum temperature increase of the water in the cell to  $10$  K and the time constant to  $10$  s. However, the value of  $Q$  is expected to be proportional to the surface area of the cell and, therefore, the square of the typical length of the cell, so that the equilibrium temperature would be inversely proportional to the square of the length. Thus, the equilibrium temperature could be much higher than  $10$  K in the small cells or channels. In addition, the time constant is expected to be proportional to the typical length of the cell. Furthermore, the rate of temperature increase is inversely proportional to the cube of the typical length of the cell. Therefore, the temperature change of the water in microchannels will be much faster than that in the cell we used. The local plasmon resonators are expected to be applicable to control the microfluid using photoacoustic generation, thermophoresis, etc.

In summary, we have demonstrated that local plasmon resonators can spatially control heat generation flexibly and efficiently and that these resonators can modulate the local temperature extremely quickly. In the future, we will measure the photoacoustic emission from local plasmon resonators.

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