Tunable Localized-Surface-Plasmon-Resonance Characteristics of Independently Prepared Ag-TiO$_2$ Particles

Noritsugu Hashimoto$^*$
Ceramics Laboratory, Industrial Research Division, Mie Science and Technology Promotion Center, 788 Higashiakuragawa, Yokkaichi, Mie, 510-0805, Japan,

Tadanori Hashimoto and Hiroyuki Nasu
Division of Chemistry for Materials, Graduate School of Engineering, Mie University, 1577 Kurimamachiya, Tsu, Mie, 514-8507, Japan

Yoshitsugu Yamamoto and Seiji Niijima
Ceramics Laboratory, Industrial Research Division, Mie Science and Technology Promotion Center, 788 Higashiakuragawa, Yokkaichi, Mie, 510-0805, Japan

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Ag and TiO$_2$ particles prepared by the evaporation-condensation method and spray pyrolysis, respectively, were mixed in N$_2$ gas flow, and then deposited on the SiO$_2$ glass substrate to form a film. Optical properties of the film thus obtained were evaluated using UV-Visible spectrophotometer and Z-scan technique. As a result, the absorption peak wavelength of Ag particles due to localized surface plasmon resonance (LSPR) was shifted toward longer wavelength side with increasing the concentration of Ti(OCH$_3$)$_4$ used as a starting material of TiO$_2$ particles. This indicates that LSPR peak of Ag particles is strongly influenced by TiO$_2$ particles. Therefore, this method is useful to develop tunable LSPR devices such as optical switches and sensors. Meanwhile, nonlinear refractive index determined by Z-scan technique was negative. [DOI: 10.1380/ejssnt.2006.566]

Keywords: Silver; Titanium oxide; Nano-particles; Localized surface plasmon resonance; Visible/ultraviolet absorption spectroscopy; Non-linear optical methods; Evaporation-condensation method; Spray pyrolysis

I. INTRODUCTION

Noble metal particles, such as Au, Ag and Cu, are much attractive for their unique optical absorption in the visible light region due to localized surface plasmon resonance (LSPR), which have been used as colored stained glasses from ancient times. Among of them, Ag particles are expected as a nonlinear optical material because of the fast nonlinear response time and the enhancement of optical nonlinearity due to LSPR.

It is well known that absorption wavelength is a function of the dielectric constant, i.e., the refractive index of the medium surrounding the metal particles. Absorption coefficient, $\alpha$, as a function of wavelength is given by the following equation,

$$\alpha = \frac{18\pi \rho d^3}{\lambda} \frac{\epsilon_2}{(\epsilon_1 + 2\epsilon_d)^2 + \epsilon_d^2}, \quad (1)$$

where $\rho$ is the volume fraction of metal, $\lambda$ is the light wavelength, $\epsilon_d$ is the dielectric constant of surrounding medium, $\epsilon_1$ and $\epsilon_2$ are the real and imaginary dielectric constants of metal, respectively. Eq. (1) has a maximum value at the LSPR wavelength under the following condition,

$$\epsilon_1 + 2\epsilon_d = 0. \quad (2)$$

TiO$_2$ is one of the most interesting materials due to the highest refractive index and potential applications.

So far, the preparation of TiO$_2$ particles by spray pyrolysis were widely studied[4]. Meanwhile, the evaporation-condensation method is a useful method to easily obtain nano-sized Ag particles, and in our previous study, optical properties of Ag particles prepared by this method were studied[5, 6]. Combining these two methods, we can easily generate nano-sized Ag-TiO$_2$ aerosol particles of various compositions by changing the particle generating conditions, and depositing on the substrate, thin film consisting of them can be obtained.

In this study, Ag and TiO$_2$ particles prepared by the evaporation-condensation method and spray pyrolysis, respectively, were deposited on the SiO$_2$ glass substrate simultaneously to obtain a film consisting of Ag-TiO$_2$ particles. Optical properties of the film thus obtained were evaluated, and the effect of TiO$_2$ particles on them was discussed.

II. EXPERIMENTAL

A. Preparation and deposition of Ag and TiO$_2$ particles

The film consisting of Ag-TiO$_2$ particles deposited on the SiO$_2$ glass substrate were prepared by the combined evaporation-condensation method and spray pyrolysis. Figure 1 shows the experimental set-up for generating and depositing of Ag-TiO$_2$ particles. First, Ag particles were generated by the evaporation-condensation method. In this method, Ag granules were heated at 900 °C in the ceramic pipe (inner diameter: 11 mm) in N$_2$ gas flow, and then cooled by cooling the copper pipe which Ag gas...
passed using water to be deposited in N$_2$ gas flow. The flow rate of N$_2$ gas was 5 L/min.

Meanwhile, TiO$_2$ particles were generated by spray pyrolysis. The preparation of a precursor solution for generating TiO$_2$ particles was as follows. Ti(OC$_3$H$_7$)$_4$ (TTIP) was stirred for 5 min, and then H$_2$O was added. TTIP concentration of the solution was 0.01 M using C$_2$H$_5$OH as a solvent. The molar ratio was H$_2$O/TTIP = 1. After further stirring was carried out for 1 h, the precursor solution was obtained. In spray pyrolysis for generating TiO$_2$ particles, diluted TTIP solutions using C$_2$H$_5$OH, from $1 \times 10^{-5}$ to $1 \times 10^{-4}$ M, were used as a precursor solution. The droplets of TTIP solution were generated using the constant output atomizer (TSI, Model 3076) with 2 L/min of N$_2$ gas flow, which were pyrolyzed at 500 °C to obtain TiO$_2$ particles in the electrical furnace. Finally, Ag and TiO$_2$ particles were mixed in N$_2$ gas flow, and then simultaneously deposited for 2 h on the SiO$_2$ glass substrate, which size was 20 × 20 mm$^2$, to form a film.

**III. RESULTS AND DISCUSSION**

**A. Characterization of Ag-TiO$_2$ films**

Figure 2 shows XRD pattern of Ag-TiO$_2$ particles deposited on the SiO$_2$ glass substrate. XRD pattern of the sample exhibited two peaks around 2θ = 38 and 44 °, which were assigned as (1 1 1) and (2 0 0) diffraction lines of Ag (JCPDS 4-783), respectively, the formation of Ag particles being confirmed. On the contrary, diffraction peaks assigned as crystalline TiO$_2$ were not observed. It is considered that TiO$_2$ particles are amorphous, or number density of them is too small to be detected. However, since both of amorphous and crystalline TiO$_2$ show high refractive index, the determination which they are crystalline or amorphous is not interested in this study.

Absorption spectrum was measured using UV-Visible spectrophotometer (Shimadzu, UV-3100) in the wavelength range between 200 and 800 nm. The nonlinear refractive index, $\gamma$, of Ag-TiO$_2$ particles was determined using Z-scan technique introduced by Sheik-Bahae et al[7]. The Z-scan setup was equipped with a Q-switched Nd:YAG laser (Spectra Physics) with generation of 10 Hz and duration of 5 ns at 532 nm. CS$_2$ was used as a reference sample to estimate an incident light intensity.
FIG. 3: Photographs of (a) Ag, (b) TiO$_2$ and (c) Ag-TiO$_2$ particles deposited on the SiO$_2$ glass substrate.

FIG. 4: FE-SEM images of (a) Ag and (b) Ag-TiO$_2$ particles which were prepared using 0 and $5 \times 10^{-5}$ M of TTIP concentration, respectively. All particles were deposited on the SiO$_2$ glass substrate.

FIG. 5: Relationship between the absorption peak wavelength of Ag particles due to LSPR and TTIP concentration of the precursor solution of TiO$_2$ particles.

between Ag particles, so that the bonding and growth of Ag particles are suppressed.

B. Linear and nonlinear optical properties of Ag-TiO$_2$ films

Absorption spectra for Ag-TiO$_2$ particles showed a peak due to LSPR of Ag particles. The relationship between the absorption peak wavelength and TTIP concentration used as the precursor solution in the preparation of TiO$_2$ particles is shown in Fig. 5. The absorption peak wavelength was shifted toward longer wavelength side with increasing the TTIP concentration over the range of $1 \times 10^{-5}$ to $5 \times 10^{-5}$ M of TTIP concentration. In addition, when TTIP concentration was above $5 \times 10^{-5}$ M, the absorption peak wavelength was almost constant.

As mentioned above, the absorption peak wavelength of metal particles was shifted due to the change of the dielectric constant of surrounding medium. Additionally, the red shift of the absorption peak wavelength of metal particles also occurred due to the change of particle size toward larger one[8] and the aggregation of metal particles[9, 10]. In the case of Ag-TiO$_2$ particles in the present study, since TiO$_2$ particles existed between Ag particles, both of the particle growth and aggregation of Ag particles less oc-
TTIP concentration / 10 M
-5
-2.0
0
-1.5
2
-1.0
4
-0.5
6
0
8
0
Nonlinear refractive index, \( \gamma \), of Ag-TiO\(_2\) particles and TTIP concentration of the precursor solution for TiO\(_2\) particles.

FIG. 6: Relationship between nonlinear refractive index, \( \gamma \), of Ag-TiO\(_2\) particles and TTIP concentration of the precursor solution for TiO\(_2\) particles.

curred compared in the absence of TiO\(_2\) particles. Therefore, the red shift of the absorption peak wavelength seen in Fig. 5 is caused by the change of dielectric constant of surrounding medium due to the increase of number density and size of TiO\(_2\) particles with increasing the TTIP concentration.

Even at low TTIP concentration used as the precursor solution in spray pyrolysis, the absorption peak wavelength of Ag particles due to LSPR was shifted. Therefore, this method is useful to develop tunable LSPR devices such as optical switches and sensors.

Nonlinear refractive index, \( \gamma \), of Ag-TiO\(_2\) particles was determined using Z-scan technique. The \( \gamma \) is plotted against TTIP concentration of the precursor solution in Fig. 6. The \( \gamma \) of Ag-TiO\(_2\) particles prepared with 1 \times 10^{-5} \text{ M} \text{ and } 2 \times 10^{-5} \text{ M} \text{ of TTIP concentration was not detected. As seen in Fig. 6, the value of } \gamma \text{ for Ag-TiO}_2 \text{ particles was negative and slightly enhanced with increasing the TTIP concentration due to LSPR because the absorption peak wavelength approached laser wavelength (532 nm) used in the Z-scan measurement. However, this absolute value of } \gamma \text{ is lower than that for Ag particles reported previously[5, 6]. Since the number density and size of TiO\(_2\) particles are increased with increasing the TTIP concentration, it is considered that the negative value of } \gamma \text{ for Ag particles, although enhanced due to LSPR, is suppressed by the positive one for amorphous TiO\(_2\) particles. Consequently, the } \gamma \text{ was not drastically enhanced.}

IV. CONCLUSIONS

The film consisting of Ag and TiO\(_2\) particles was prepared by the combined evaporation-condensation method and spray pyrolysis. The absorption peak wavelength of Ag-TiO\(_2\) particles due to LSPR was shifted longer wavelength side, from 470 to 520 nm, as TTIP concentration of the precursor solution used in spray pyrolysis was increased. Since the absorption peak wavelength is shifted and TiO\(_2\) particles strongly affect on optical properties of Ag particles even at low TTIP concentration, this method is useful for developing tunable LSPR devices. However, the enhancement of \( \gamma \) was not achieved.

[1] Y. Hamanaka, A. Nakamura, S. Omi, N. D. Fatti, F. Vallée and C. Flytzanis, Appl. Phys. Lett. 75, 1712 (1999).
[2] K. Uchida, S. Kaneko, S. Omi, C. Hata, H. Tanji, Y. Asahara, A. J. Ikushima, T. Tokizaki, and A. Nakamura, J. Opt. Soc. Am. B 11, 1236 (1994)
[3] G. Mie, Ann. Phys. 25, 377 (1908).
[4] W-N. Wang, I. W. Lenggoro, Y. Terashi, T. O. Kim and K. Okuyama, Mater. Sci. Eng. B 123, 164 (2005).
[5] N. Hashimoto, T. Hashimoto, H. Nasu and K. Kamiya, J. Ceram. Soc. Japan 112, 204 (2004).
[6] N. Hashimoto, Y. Yamamoto and S. Niijima, e-J. Surf. Sci. Nanotech. 3, 120 (2005).
[7] M. Sheik-Bahae, A. A. Said, T. H. Wei, D. J. Hagan and E. W. Van Stryland, IEEE J. Quantum Electron. 26, 760 (1990).
[8] L. Yang, G. H. Li and L. D. Zhang, Appl. Phys. Lett. 76, 1537 (2000).
[9] S. Norrman, T. Andersson C. G. Granqvist and O. Hunderi, Phys. Rev. B 18, 674 (1978).
[10] M. Quinten and U. Kreibig, Surf. Sci. 172, 557 (1986).