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Author(s)	Ochiai, Takao; Isozaki, Katsuhiko; Pincella, Francesca; Taguchi, Tomoya; Nittoh, Koh-ichi; Miki, Kazushi
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## Plasmon-Resonant Optics on an Indium–Tin-Oxide Film for Exciting a Two-Photon Photochromic Reaction

Takao Ochiai<sup>1,2</sup>, Katsuhiro Isozaki<sup>1,3\*</sup>, Francesca Pincella<sup>1,2</sup>, Tomoya Taguchi<sup>1,2</sup>, Koh-ichi Nittoh<sup>1</sup>, and Kazushi Miki<sup>1,2\*</sup>

<sup>1</sup>National Institute for Materials Science (NIMS), Tsukuba, Ibaraki 305-0044, Japan

<sup>2</sup>Department of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan

<sup>3</sup>International Research Center for Elements Science, Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

E-mail: kisozaki@scl.kyoto-u.ac.jp; MIKI.Kazushi@nims.go.jp

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Two-dimensional arrays of gold nanoparticles (AuNPs) as localized surface plasmon-resonant (LSPR) optics on a transparent conductive layer of indium–tin-oxide (ITO) were successfully fabricated. The typical surface coverage of the 10 nm sized AuNPs is over 87% for on ITO film roughness of  $\pm 0.2$  nm. The LSPR wavelength is tunable in the range of 622–905 nm. By adjusting the LSPR wavelength to 905 nm at peak, two-photon photochromic reaction of diarylethene derivative in solution phase was demonstrated with irradiation by an incoherent near-infrared light in the range of 0.017–0.033 W/cm<sup>2</sup> instead of a laser, thanks to the AuNP two-dimensional array. © 2013 The Japan Society of Applied Physics

Gold nanoparticles (AuNPs) have been studied extensively for application to nanophotonics because their localized surface plasmon-resonance (LSPR) exhibits unique characteristics of near-field light, such as the localization of light below diffraction limits and the generation of enhanced electromagnetic fields, called “hot spots”, in the gap between closely spaced AuNPs.<sup>1–6</sup> For one application of nanophotonics to photochemistry, it was reported that multiphoton excitation proceeds at hot spots similarly to when irradiated by laser.<sup>3–7</sup> In optoelectronic devices, chemical modification of the surface of transparent conductive materials<sup>8–12</sup> offers outstanding potential for the development of functional electrodes. Indium–tin-oxide (ITO) is one such transparent conductive material and is extensively used in various applications such as solar cells,<sup>8,11,13</sup> organic light-emitting diodes (OLEDs),<sup>14,15</sup> and electroluminescent (EL) devices.<sup>8</sup> Surface modification of ITO with optical layers<sup>2,12,16</sup> enables the surface to absorb irradiated light and emit light of various wavelengths. Thus, surface modification of ITO substrates with closely spaced AuNPs in two dimensions (2D) is expected to increase the density of hot spots on transparent conductive electrodes showing characteristic near-field optical properties such as multiphoton excitation.

Recently, we demonstrated a new technique, called the hybrid self-assembly method, for chemically immobilizing large-area ( $>1$  cm<sup>2</sup>) AuNP 2D arrays as near-field light sources on gold films and evaluated the tunability of their LSPR bands as near-field optics.<sup>6</sup> In the hybrid self-assembly method, we manipulate both the size of AuNP in the range of 5–100 nm and the gap between AuNP neighbors in the range of 1–3 nm, and therefore should be able to achieve a high density of hot spots in the infrared–visible light region on the ITO. In this study, we succeeded in using the method to immobilize AuNP 2D arrays on the ITO film [Fig. 1(a)]. By adjusting the LSPR wavelength to 905 nm at peak to use 74 nm sized AuNP, two-photon photochromic reaction of diarylethene derivative in solution phase was demonstrated with irradiation by incoherent near-infrared (NIR) light [Fig. 1(b)]. The same photochromic reaction in solid phase induced by two-photon absorption (TPA) with gold nanostructures was first confirmed by Tsuboi et al. with NIR CW laser (808 nm, 0.1–4.0 W/cm<sup>2</sup>) irradiation.<sup>5</sup> Later, photochromic reaction in solution phase with coherent NIR laser irradiation (800 nm, 80 MHz, 100 fs pulse, 9 MW/cm<sup>2</sup>) has

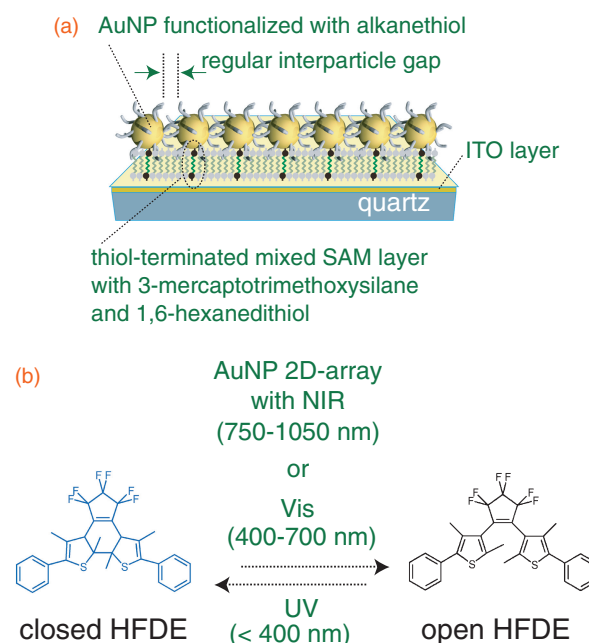
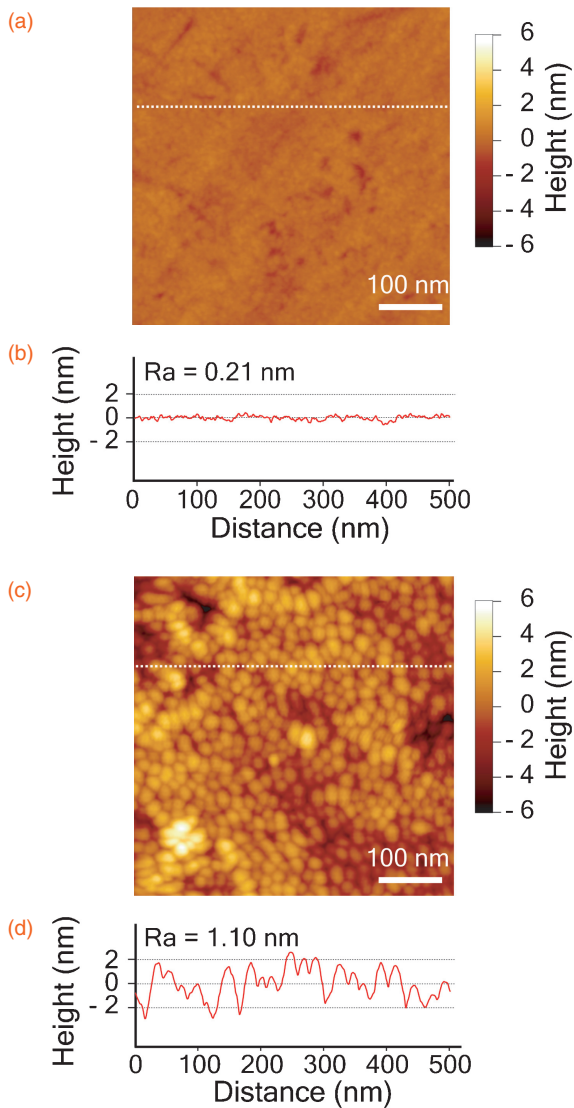


Fig. 1. (a) Sample structure of AuNP 2D array on ITO. (b) Normal and TPA-induced photochromic reaction of HFDE.

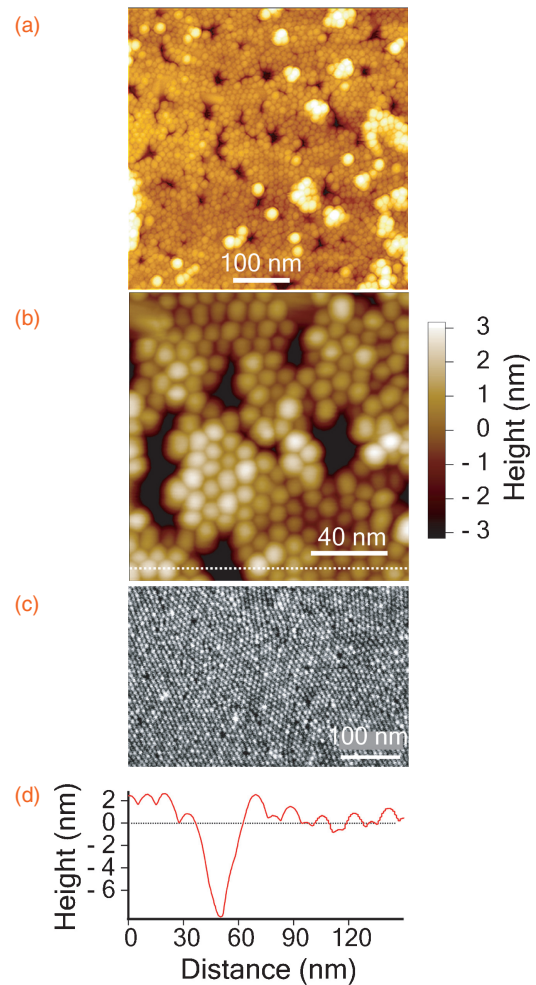
been reported<sup>7</sup>) without evidence of two-photon dependence of the reaction process. In the present study, by irradiation with incoherent NIR light in the range of power density of 0.017–0.033 W/cm<sup>2</sup>, instead of laser, we achieved solution-phase photochromic reaction and confirmed two-photon dependence. This study shows that the simple concept of two-photon excitation with not a single hot spot but a high density of hot spots can be effectively applied to TPA-driven solar cells, OLEDs, EL devices, and optoelectronic devices.

To enhance TPA, we used large-area AuNP 2D arrays on ITO substrates [Fig. 1(a)]. Optimization experiments revealed that the best parameters for electrophoresis-based self-assembly of AuNPs on ITO films are similar to those used for the deposition of AuNP 2D arrays on Au films.<sup>6</sup> The ITO-film-coated quartz substrates were sequentially functionalized with 3-mercaptoptrimethoxysilane and 1,6-hexanedithiol, and used as cathodes for the electrophoresis: a voltage of 1.0 V was applied to a colloidal AuNP solution ( $5.7 \times 10^{13}$ /mL) in *n*-hexane using plastic-formed carbon electrodes as anodes, where the interelectrode distance was



**Fig. 2.** (a) AFM images of sputtered ITO (10.7 nm)/quartz (0.625 mm) and (b) height profile along the white dotted line in image (a). (c) AFM image of commercially available ITO (154.6 nm)/glass (0.7 mm) substrate surfaces and (d) height profile along the white dotted line in image (c). The scale bar is 100 nm.

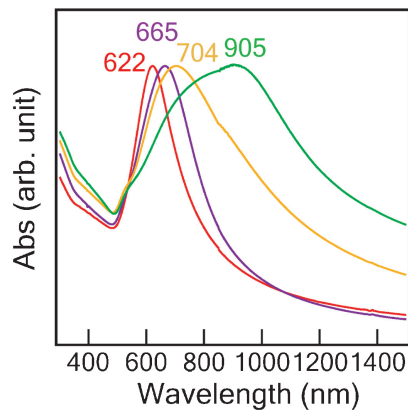
1.2 mm. The flatness of ITO films is an important factor in the fabrication of large-area AuNP 2D arrays because the roughness should be less than the particle diameter. We examined two types of ITO film. One was a sputtered ITO film (thickness: 10.7 nm, electrical resistivity:  $4.1 \times 10^{-3} \Omega \text{ cm}$ ) fabricated by sputtering an ITO target ( $\text{In}_2\text{O}_3$ -10 wt%  $\text{SnO}_2$ ) onto a quartz substrate (thickness: 0.625 mm), and the other was a commercially available ITO/glass substrate (thickness of ITO:  $154.6 \pm 20 \text{ nm}$ , thickness of glass:  $0.7 \pm 0.05 \text{ mm}$ ) purchased from Geomatec. Atomic force microscopy (AFM) observations (Asylum Research Cypher AFM) showed that the flatness of the surface of the sputtered ITO films (roughness of  $\pm 0.21 \text{ nm}$ ) was higher than that of the commercially available ITO substrate (roughness of  $\pm 1.10 \text{ nm}$ , Fig. 2). The sputtered ITO films showed higher coverage than the commercially available substrate in the electrophoresis-based self-assembly of AuNPs. For comparison, we fabricated AuNP 2D arrays by the self-assembly of dodecanethiol-coated AuNPs with a radius of 10 nm,



**Fig. 3.** (a) AFM image of dodecanethiol-coated 10 nm AuNP 2D array on the sputtered ITO (10.7 nm)/quartz (0.625 mm) substrate, (b) its magnification, and (c) corresponding SEM image. (d) Height profile along the white dotted line in (b).

and found that the 10 nm AuNP 2D arrays gave 87.1% coverage for sputtered ITO films and 75.6% for the commercially available ITO substrate [Fig. 3(a)]. Thus, the key to successful fabrication of high-coverage AuNP 2D arrays on the ITO film is to reduce the roughness of the ITO surface. From AFM and SEM images [Figs. 3(b) and 3(c)], the radius of the 10 nm AuNPs and the interparticle gap distances were identified to be 9.0 and 2.4 nm, respectively, which are similar to those obtained for AuNPs fabricated on Au films.<sup>6)</sup> The AFM height profile [Fig. 3(d)] indicates that the array of AuNPs was flat and the height of the 10 nm AuNP 2D array was ca. 10 nm; these values coincide well with those for a structure constructed using dodecanethiol-coated AuNPs with a radius of 9.0 nm.

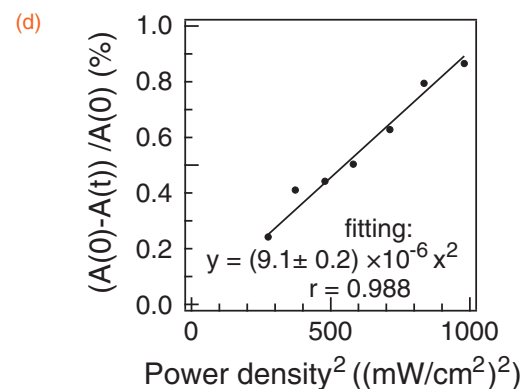
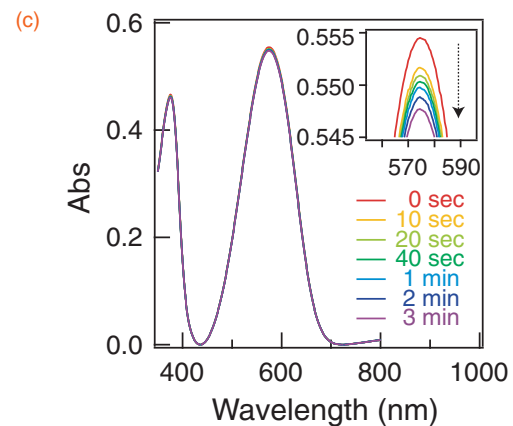
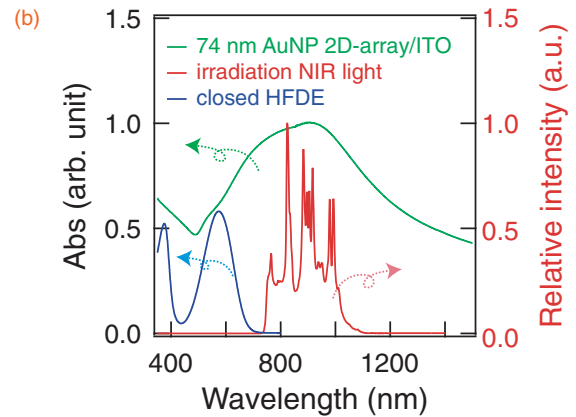
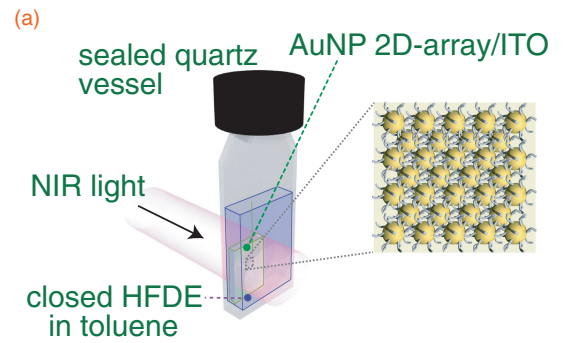
To determine the optimum structure of AuNP 2D arrays as a near-field light array of light sources for the TPA-based excitation of 1,2-bis(2,4-dimethyl-5-phenyl-3-thienyl)-3,3,4,4,5,5-hexafluoro-1-cyclopentene (HFDE; Tokyo Kasei), which was used in this study because it undergoes a very fast and reversible photochromic reaction [Fig. 1(b)],<sup>17)</sup> we fabricated various AuNP 2D arrays showing different LSPR wavelengths based on the particle size and interparticle gap distance.<sup>6,18,19)</sup> 15, 38, 56, and 74 nm AuNPs were



**Fig. 4.** Extinction spectra of 15 nm (red, 622 nm at peak), 38 nm (purple, 665 nm at peak), 56 nm (orange, 704 nm at peak), and 74 nm (green, 905 nm at peak) particle-size AuNP 2D arrays on the sputtered ITO (10.7 nm)/quartz (0.625 mm) substrates.

synthesized by the seed growth method<sup>20)</sup> and functionalized with 1-dodecanethiol. All these AuNPs were self-assembled and immobilized on substrates coated with a sputtered ITO film to form 2D arrays. Extinction spectra (JASCO V-670) of these AuNP 2D arrays exhibited LSPR bands at 622, 665, 704, and 905 nm, respectively (Fig. 4), revealing that the LSPR wavelength is tunable in the range of 622–905 nm and its half width is 150–400 nm. From these spectral analyses, the 74 nm AuNP 2D array was chosen as the best candidate for TPA-based excitation of the photochromic reaction of HFDE having its absorption band at 435–725 nm because its LSPR<sub>max</sub> is localized in the NIR range, although shoulders in the lower wavelength region arise from the small domains such as AuNP dimer, trimer, or oligomer, in addition to the main peak originating from the large domains of the AuNP 2D array. Numerical simulation of simple dimer and trimer models of 74 nm AuNPs by the discrete dipole approximation (DDA) method<sup>21)</sup> clarified that “hot spots” are generated in gaps between neighboring AuNPs and, judging from the irradiation-light-wavelength dependence of the simulated electric field of the hot spots, the LSPR light was confirmed to be red-shifted. Thus, the 74 nm AuNP 2D array is expected to act as a large-area near-field light array for inducing the TPA photochromic reaction of HFDE. The details will be published independently.

Two-photon photochromic reaction of HFDE in solution phase was demonstrated by irradiation with incoherent NIR light instead of laser. 2D arrays of dodecanethiol-coated AuNPs with a radius of 74 nm immobilized on ITO substrate (total thickness with glass substrate: 0.625 mm) were immersed in a toluene solution of the closed form of HFDE (closed HFDE, 1.0 mM, 0.1 mL) charged in a screw-capped quartz cell with an optical path of 1.0 mm [Fig. 5(a)]. The substrate was irradiated by NIR light (Asahi Spectra MAX-302, 750–1050 nm) from the backside of the AuNP 2D array in a dark room. As the NIR light was irradiated, the blue color of the closed HFDE gradually disappeared as it was converted to colorless open HFDE [Figs. 5(b) and 5(c)], even though there was no absorption band of closed HFDE in the irradiated region. The resulting solution was then reconverted to closed HFDE by UV irradiation (<400 nm) with negligible spectral changes. Of course, in the case of



**Fig. 5.** (a) Schematic illustration of experimental setup for TPA-induced photochromic reaction. (b) UV-vis absorption spectrum of closed HFDE in toluene (1.00 mM, blue line), spectrum of incoherent NIR light source (red line), and extinction spectrum of 74 nm particle-size AuNP 2D array (green line). (c) Time-course UV-vis absorption spectra of solution of HFDE during TPA-induced photochromic reaction. Inset: enlargement of the time-course UV-vis absorption spectra around the maxima at 575 nm. (d) Reaction yields for 1 min as a function of the square of power density.



the ITO substrate without the AuNP 2D array, no spectral changes were observed under NIR light irradiation. These results suggest that the photochromic reaction of HFDE is induced by TPA with the enhanced electromagnetic field of the AuNP 2D array. To investigate the origin of the photochromic reaction induced by the AuNP 2D array, we examined the dependence of the photochromic reaction yield on irradiation power [Fig. 5(d)]. The reaction yield obtained from extinction spectra showed a linear dependence on the square of power density in the range of 0.017–0.033 W/cm<sup>2</sup>, clarifying that this photochromic reaction proceeds depending on the TPA process.<sup>4)</sup>

In summary, we successfully demonstrated TPA-driven photochromic reactions by using incoherent NIR light irradiation instead of laser, thanks to the AuNP 2D array on the ITO. The transparency of the ITO films and the TPA property of the AuNP 2D arrays enabled TPA-driven photochromic reactions. The TPA excitation wavelength of the AuNP 2D arrays was adjusted by tuning their LSPR wavelengths on the basis of particle size using a previously reported method.<sup>6)</sup> Microscopic observations of the AuNP 2D arrays revealed that the flatness of the ITO film was the key parameter in ensuring the formation of large-area AuNP 2D arrays. These results indicate the applicability of AuNP 2D arrays, which act as near-field light sources, as functional transparent electrodes for TPA-driven solar cells, OLEDs, EL devices, and optoelectronic devices.

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Professor H. Takaya (Kyoto University) for their helpful discussions, and Dr. S. Nishiyama (NIMS) for technical advice. T.T. thanks the Japan Society for the Promotion of Science for the Young Scientist Fellowship. SAXS measurements were performed at BL40B2, SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Grant Nos. 2010B1744, and 2012A1575).

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