# Study on plasmon induced electron injection mechanism in Au-$TiO_2$ nanoparticle system (1) --lifetime observation of excited states by fs laser pump-probe PEEM--

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**(Introduction)** While $TiO_2$, an excellent photo-catalyst, is desired to become a good material for solar cell, the photocurrent efficency is low because of its large bandgap of 3.2 eV. Only UV lights can excite electrons to conduction band, and visible and near infrared lights which occupy large portion of the sun shine energy can not contribute to creating free electrons.

To overcome this shortcoming of $TiO_2$, Au-$TiO_2$ nanoparticle (NP) system has been studied extensively (ref). In metal-NPs, resonance frequency of plasmon shifts to visible region, and they can be very good materials for solar cells. In Au-$TiO_2$-NP system, visible lights are absorbed by Au-NP to create plasmons, and electrons excited by plasmons in Au-NP trnasfer to $TiO_2$-NP, and electrons are separated from holes in $TiO_2$-NP. Previous reseraches studied electron transfer by measuring photocurrent. But it was difficult to evaluate diffusion of electrons in $TiO_2$-NP which is important for improving the performance, because of lacking spatial resolution. We started a research of studying electron injection mechanism in Au-$TiO_2$ nanoparticle system by using a PEEM whcih has a 30-nm spatial reoslution. At the beginning of the research, we confirmed insulators can be observed under PEEM with no problem.

**(Experiment)** A laser pulse from a fs laser system was split into two beams and combined in a Mach-Zehnder interferometer with varied delay time between two pulses,and irradiated a sample in a vacuum chamber. A droplet including Au particles of 10-nm nominal size dispersed by surfactant was dropped on powder of $TiO_2$ particles of 100-nm nominal size on a Si wafer of 10 mm size, and the sample was baked at 500degC. Electrons ejected from the sample by the fs laser irradaition was imaged by PEEM.

**(Result)** Figure 1 shows the laser intensity illuminating the sample observed by scanning the delay time of two pulses. Ringing frequency of 390-nm is a half of the wavelength of the fs laser. The envelope shows that the pulse width was about 10-fs. PEEM image with Field of View of 10 μm is shown in Fig.2. Brightness of the image as a function of the delay time of two fs laser pulses is shown in Fig.3.We see two decay components. One component was as short as the laser pulse width and the other was about 20fs.

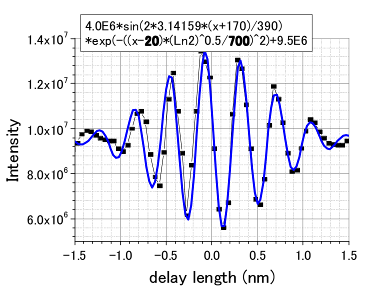


Fig.1:Laser intensity to chamber

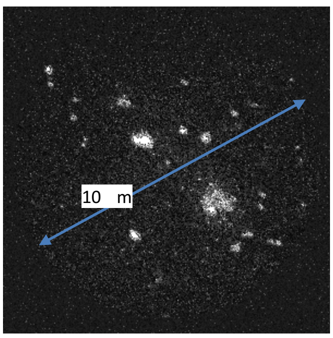


Fig.2: PEEM image

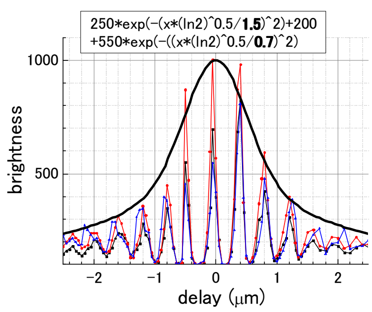


Fig.3; Brightness of spots

(ref) L.Du *et al.* ; J.Photochem. Photobio. C : Photochem Reviews **15** (2013) 21