Observation of plural photon numbers in multiphoton ionization of TiO_2 nanoparticles

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(Introduction) By using a photoemission electron microscope (PEEM) having a spatial resolution of 40-nm, we have been studying Au nanopartice (NP)-TiO_2 NP system in order to understand electron dynamics for realizng high efficiency sollar cell (ref.1). Multiphton ionization gives information on binding energy of electron source states and lifetime of excited electrons. Most of previous works reported single number multiphoton. In this paper, we report observation of plural photon-numbers in multiphotona ionization of TiO_2.

(Experimental result) TiO_2 particles of 100-nm nominal size were spread on a Si wafer and baked at 500degC for one hour before loading to vacuum chamber of PEEM. A 150 fs pulse from a Ti:S laser irradiated a sample, and particles were observed by PEEM. Fig.1 shows brightness of bright 5 particles under 810 nm laser excitaion. At power lower than 200mW, brightness of all particles, including particles not shown here, showed 5-photon slope. At shorter laser wavelength, 4-photon slope was observed and the slope of non-linear increase of brightness made a jump between 790 nm and 810 nm.

(Discussion) From the wavelength of photon number jump, as show in Fig.2, the binding energy of electron source states is estimated to be 6.2 eV from vacuum level. This vaue is smaller than the calculated ionization energy of 7.8 eV for Rutile and 8.3 eV for Anatase (ref.2). So, this level should be attributed to Ti 3d defect sates which lie at 0.8 eV below Fermi level (ref.3).

In. Fig.1, we notice brightness enhancement at high laser power. There are many reports of brightness saturation but the observed is brighntess enhancement. The other interesting thing is that the brighntess enhancemnt was clear only for brightest particles.

Enhanced brightness at high power can be fitted with 10-photon ionization for all wavelengths from 710 nm to 850 nm. 10-photon ionization with 710 nm light suggests that the binding energy of electron surrce states is larger than 15.7eV. But this value is too much larger than the calculated ionization energy of 8.3eV for Anatase. Presently, we have no explanation of the observed 10-photon slope at high laser power.

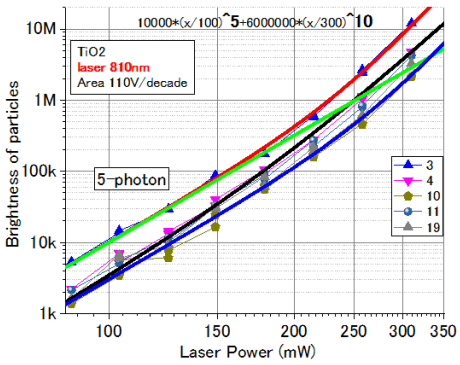

Fig.1: Brightness of particles as a function of laser power

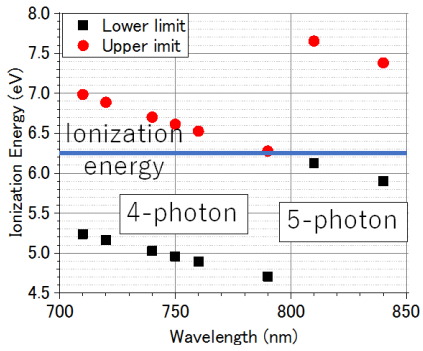

Fig.2: Number of multiphoton slope

References

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(ref.3) Adam Argondizzo *et al*, *Physical Review* B **91**, 155429 (2015)