Ionization energy of individual TiO_2 nanoparticles observed by PEEM

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(Introduction) TiO_2 is an important material in many applications such as solar cells and photocatalysis. There is a huge number of reports on the electronic structure of TiO_2, but none of them observed individual nano-particles (NP) and values are ensemble averages of NPs. We are trying to observe the variation of electronic states among NPs using a photoemission electron microscope (PEEM) having a spatial resolution of 40-nm, by which we want to get information for deeply understanding electron dynamics (ref.1). Electrons to be detected by PEEM are excited through multiphoton ionization using a femtosecond laser. From the photon number for ionization, we can evaluate the ionization energy. In this paper, we report there were two groups of TiO_2 NPs having a different ionization energy. **(Experimental result)** TiO_2 NPs of 100-nm nominal size were dispersed on a Si wafer and baked at 500degC for one hour before loading to the vacuum chamber of PEEM. A 150 fs pulse Ti:S laser irradiated a sample. Fig.1 shows one example of PEEM images of TiO_2 NPs. We gave numbers to 72 NPs. TiO_2 NPs were observed at various laser wavelengths by changing laser power.

As shown in Fig.2 for the case of 790nm laser irradiation, for most of NPs, brightness increased with 4 th power of laser power. However, some particles showed 5-photon ionization. In Fig.2, the brightness was divided by I^4 for easy evaluation of the slope near 4.

Table I summarizes photon number of multiphoton ionization at 4 laser wavelengths. For most of the particles, photon number jumped between 790 nm and 810nm, from which the ionization energy is estimated to be larger than 6.1eV (1.53eVx4) and smaller than 6.3eV (1.57x4). For 16 NPs (#3, #6, and so on) among 72 NPs, the ionization energy was larger than 6.3eV (1.57eVx4) and smaller than 6.5eV (1.63eVx4).

(Discussions) There are many reports of the ionization energies of TiO_2. All reports the value larger than 7eV. However, for example in the case of photoelectron yield (PY) spectroscopy, these values are the intersection of the tangent to the spectra with the baseline and weak signal extended down to 6eV (ref.2). Therefore, our observed values may correspond to ionization of defects level in the bandgap generating a weak signal in PY.

The observed two groups having a different ionization energy may have a different density of defects or may have a different facet, or due to different work function caused by unknown other reasons.

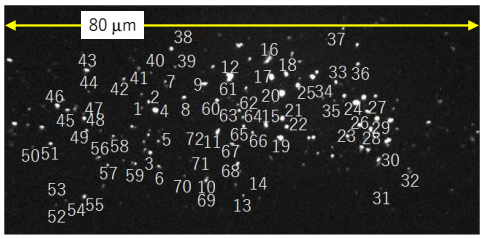

Fig.1: TiO_2 NPs observed with PEEM.
Field of view is 80µm

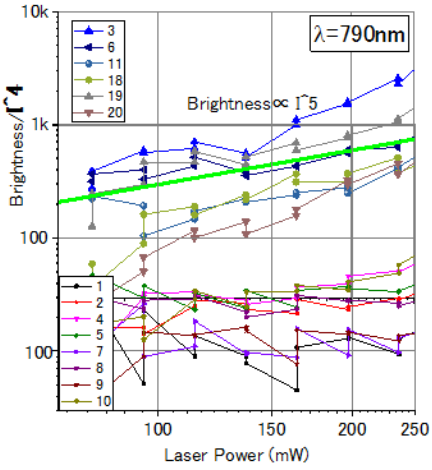

Fig.2: Brightness of NPs as a function of laser power.

Particle numbers	760nm (1.63eV)	790nm (1.57eV)	810nm (1.53eV)	840nm (1.48eV)
3, 6,11-14, 18-20,28,30-32, 54-56	4	5	5	5
1,2,4,5,7-10,15-17, 21-27,29,33-53, 57-72	4	4	5	5

Table I: Slope of the curve of brightness vs laser power.

References

(ref.1) Bochao Li, *et al.*, *65th JSAP 2018 Spring meeting*, 17a-G202-8 (2018/03/17)
(ref.2) T. Toyoda *et al.*, *RSC Adv.* **5**, 49623 (2015)