Theory of hot electrons revealing the excited state in the conduction band of a single cluster of TiO_2 nanoparticles

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(Introduction) In solar cells and catalytic reactions, highly energetic electrons, called as "hot electrons", are transferred over a potential barrier, and high efficiency generation of hot electrons is one of the most important issues. If there is an excited state, a potential barrier is lowered, leading to a great enhancement of the electron flow. However, no previous works on nanomaterials discussed excited states in the conduction band. We disclose a novel diagnostic of the excited state. By applying the derived theory to the experimental data of TiO_2 nanoparticles (NPs), the e_g and t_{2g} states in the conduction band are revealed.

(Theory of hot electrons) The energy width of electrons just after photo-excitation will be narrow but they are instantly thermalized in 10 fs or so according to references. We assume the energy distribution of photo-excited electrons in an excited state becomes the Boltzmann distribution by thermalization as shown in Fig.1. Most of the absorbed n-photon energy is used to excite the electron to the excited state, and the excess energy of the photo-excited electron above the ground state of the excited state $E_k = nh\nu - E_G - E_B$, is stored in the electron gas as a heat. Here, $h\nu$ is the one-photon energy, and E_G is the energy difference of the ground state of the electron gas from the valence band top. E_B is the "binding energy" of the excited electron measured "from the valence band top". The temperature is given by $kT = (2/3)(nh\nu - E_G - E_B)$ and the number of electrons ejected to the vacuum is given by $N_{emit} = \{(\alpha N_{ph})^n/n\} N_{e0} \exp(-\Delta E/p(nh\nu - E_G))$, where, α is the one-photon absorption efficiency, N_{ph} is the number of photons irradiating the NP, N_{e0} is the number of electrons contributing to the excitation, ΔE is an energy difference of the vacuum level and the ground state of the excited state. N_{e0} and parameter p are determined by the density of states of the valence band.

(Revealing the excited state) TiO_2 NPs dispersed on a Si wafer irradiated by laser pulses of 150 fs pulse width were observed by PEEM. The wavelength dependence of brightness of two NPs is shown in Fig.2. Fitting the derived equation gave the values of E_G =3.6 eV and 5.7eV for two NPs. From ref.1, 3.6 eV corresponds to the direct band gap and 5.7eV corresponds to the transition from the O2p to the Ti3d e_g state both at X point. Parameter p and the ionization energy $\Delta E + E_G$ were assumed as 2/9 and 7.5eV, respectively.

(**Discussion**) The derived theory is the first theory of hot electrons. The excited states of a single cluster of TiO_2 NPs were observed for the first time. The difference of E_G values for two NPs is attributed to the different density of defect states in two NPs. It was not discussed in previous works, but the essential point of high catalytic activities in nanomaterials can be the generation of high lying excited states caused by defects generated by high stress at the surface of small curvature nanomaterials.

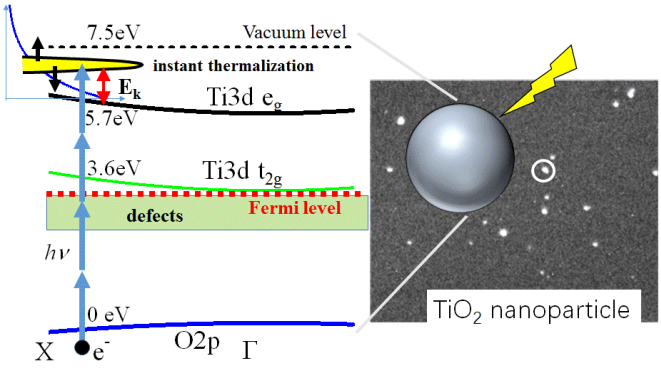

Fig.1: Model of hot electrons.

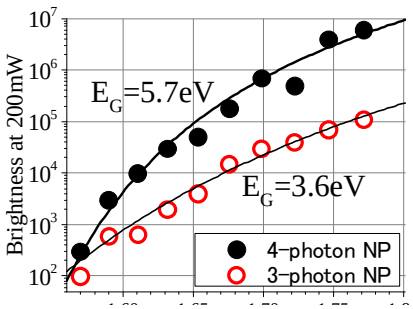

Fig.2: Wavelength dependence of Brightness of NPs as a function of laser power.

Ref.1. N. Daude, C.Gout, and C. Jouanin, Phys. Rev. B **15**, 3229 (1977)