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Bandgaps and Surface Inter-Band States in Photocatalysts with High Energy Resolution EELS.

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Photocatalysts have potential applications for solar fuel generation through water splitting [1]. The bandgap and inter-band states of the semiconductors significantly affects the performance and efficiency of the catalysts. Recent advances in STEM EELS monochromation now allow for routine ultra-high energy resolution of 15 meV or better in the low-loss region [2]. The ability to now correlate atomic structure and electronic structure in the low-loss and bandgap region of the energy-loss spectrum represents a powerful tool for characterization of electronic and optical properties of nanomaterial such as the high surface area, particulate systems that are generally used as catalysts. The band structure can vary among different nanoparticles depending on particle sizes, facets and also at the surfaces/interfaces of the semiconductors where charge transfer and photocatalytic reactions take place. With the innovation of high energy resolution EELS, it is possible to tackle the issues mentioned above by investigating the bandgap and the fine electronic structures inside the gap at the nano-level.

This study focuses on TiO_2 and Ta_2O_5 which are both UV absorption photocatalysts due to their large bandgaps. TiO_2 is relatively abundant with simple crystal structures while Ta_2O_5 is very efficient with more complicated structures. Four different samples were obtained: anatase TiO_2 (HP), Ta_2O_5 (HP), Ni/TiO_2 (LP) and NiO/Ta_2O_5 (LP). TiO_2 (HP) and Ta_2O_5 (HP) represent high purity TiO_2 and Ta_2O_5 nanoparticles which were prepared following hydrothermal/solvothermal methods. Ni/TiO_2 (LP) was obtained first by wetness impregnation on low purity commercial anatase TiO_2 which are hundreds of nm in size then reduced @500 ℃ in flowing 5% H_2/Ar for 2hrs [3]. It is used as a model of metal co-catalyst loaded on semiconductor to study the band structures at the interfaces. NiO/Ta_2O_5 (LP) as a model of semiconductor-semiconductor photocatalyst was prepared also first by impregnation but then oxidized @500 ℃ in flowing O_2 for 2hrs [4]. Low-loss EELS was carried out on a monochromated and aberration-corrected NION microscope operated at 60 kV with dispersions of 5 meV or 2 meV per channel. The energy resolution was better than 25 meV.

Fig.1 shows the bandgap edges of Ta_2O_5 (HP) and TiO_2 (HP) acquired under aloof beam conditions in which the electron beam was positioned at about 5 nm away from the particle surfaces. The measured values of Ta_2O_5 (HP) and TiO_2 (HP) bandgap from more than 6 different spectra are 4.50 eV $\pm$ 0.02 eV and 3.60 eV $\pm$ 0.01 eV respectively. The bandgap is measured by extrapolating the straight portion of the fitted curve to the x axis. For anatase, the EELS measurement of 3.60 eV is larger than the well-known ~3.2 eV but close to the recent theoretical calculation and experimental data [5]. Fig.1b also shows the bandgap of anatase increases to 3.71 $\pm$ 0.03 eV as the Ti in the particle was reduced from Ti^{+4} to Ti^{+3} by the electron beam (Figure 1b insertion) which is contradictory to conventional optical measurements showing a narrower bandgap for reduced TiO_2. The reason is not clear at this stage. On Fig. 2, inter-band states were clearly observed when the beam was on the surfaces of bare Ta_2O_5 and TiO_2 of the NiO/Ta_2O_5 (LP) and Ni/TiO_2 (LP) samples. Distinctive interstates peaks were at 1.13 eV,

2.14 eV and 2.66 eV for Ta_2O_5 and 2.08 eV, 2.37 eV and 2.85 eV for TiO_2. The peaks are only observed on the surface of the particles and they vanish when the beam is in the bulk Ta_2O_5 or TiO_2. Those states are believed to be related to the oxygen vacancies produced from the high temperature reduction and/or impurities segregated to surfaces in the commercial TiO_2 or Ta_2O_5 after high temperature heat treatment. The energies of these inter-band states vary among different particles depending on their local morphology and impurity concentrations. Peaks associated with different oxygen vacancy concentrations were also observed. More experimental data with theoretical simulation to explore the complicated electronic band structures of these photocatalyst materials will be presented.

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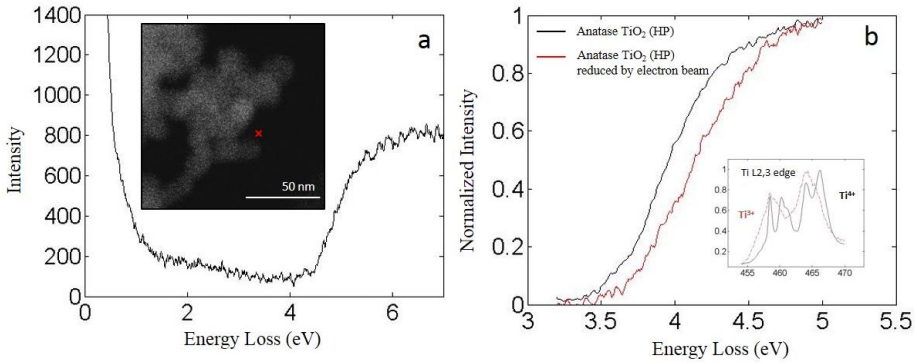

Figure 1: a) Low-loss EELS with insertion of STEM image showing beam was near surface of Ta_2O_5 (HP) particles; b) Bandgap edge from anatase TiO_2 (HP) with insertion of Ti $L_{2,3}$ edges before and after reduction by electron beam.

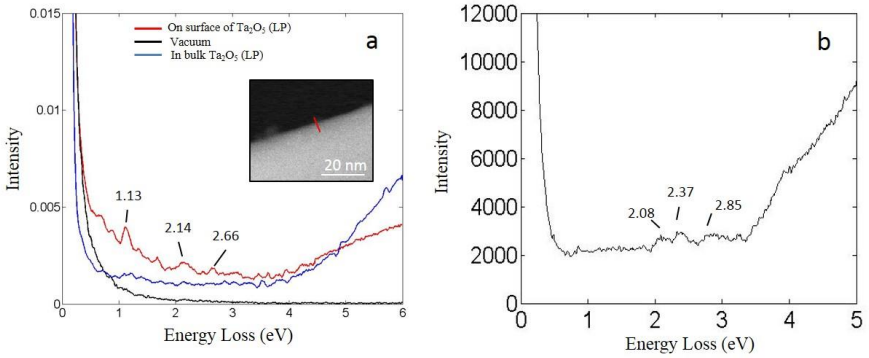

Figure 2: a) Inter-band states on surface of Ta_2O_5 (LP) and low-loss EELS of vacuum. The insertion shows where the surface spectra were taken; b) Inter-band states on surface of TiO_2 from Ni/TiO_2 (LP) sample.

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