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Electronic structure of inverse opal- and nanoparticulate- TiO_2 electrodes

One of the main factors determining the photovoltaic performance in sensitized solar cell is the morphology of the TiO_2 electrode. Using a suitable morphology can lead to improvements in the photovoltaic conversion efficiency. The present study focuses on a comparison between the electronic structure of inverse opal (IO)- and nanoparticulate (NP)- TiO_2 electrodes. A higher open circuit voltage, V_{oc} , was observed with IO- TiO_2 electrodes compared to conventional NP- TiO_2 electrodes. It appears that fundamental studies are needed to shed light on the underlying physics and chemistry governing the enhancement of V_{oc} . Optical absorption measurements by the photoacoustic spectroscopy showed that indirect and direct transitions can be observed in IO- and NP- TiO_2 . The indirect bandgaps of IO- and NP- TiO_2 are similar to each other (~ 3.2 eV) in good agreement with previously reported, and the direct bandgaps of them are ~ 3.6 eV and ~ 3.5 eV, respectively, indicating difference in the electronic structure. There is a possibility that the density of states in the conduction band of IO- TiO_2 is larger than that of NP- TiO_2 . Analysis of the Urbach tail shows that there is a higher exciton-phonon interaction in IO- TiO_2 than in NP- TiO_2 . Indirect photoluminescence (PL) and exciton PL can be observed. Also, PL due to oxygen vacancies was observed. The PL spectra suggest difference in the valence band structure between IO- and NP- TiO_2 . The position of valence band maximum for IO- TiO_2 is higher than that for NP- TiO_2 measured by photoelectron yield spectroscopy, indicating that the surface of IO- TiO_2 is polarized with more positive dipole moment toward the vacuum level than that of NP- TiO_2 . Hence, the formation of a double layer in the former is different from that in the latter due to the differences in the formation of oxygen vacancies, suggesting a correlation with the increased V_{oc} in sensitized solar cells.

