Zinc-doping in TiO_2 Films to Enhance Electron Transport in Dyesensitized Solar Cells under Low-intensity Illumination

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Dye-sensitized solar cells (DSSCs) have been investigated extensively because of their advantages, such as high efficiency, low cost, environment-friendliness, low incidentlight-angle dependence, and so on. For DSSCs under low-intensity illumination, however, the concentration of photogenerated electron is low and the rate of charge transfer in TiO_2 media, as well as that of charge recombination, is predominantly governed by the density of trap states in TiO_2. The injected electrons may be multiply captured by the trap states in the diffusion process, hence trapping/detrapping event is a dominant mechanism for electron transport in DSSCs. To promote electron transport, a previous study reported that dopant introduction was able to increase the n-type carrier concentration of TiO_2 films and thus to reduce the film resistance. We thereby consider heteroatom-doping an effective way to enhance the electron mobility in DSSCs.

In this study, we present our findings of enhancing electron mobility in DSSCs by doping the TiO_2 films with Zn ion, which has a size similar to that of Ti ion and an oxide structure intrinsically with high donor density. We develop a method to introduce Zn substituting for Ti, thus to effectively. disperse Zn in the TiO_2 films. A homogeneous distribution of Zn ions in the TiO_2 films will minimize the defect states resulting from this substitution. The Zn-doping is shown to significantly alleviate the decay of the light-to-electric energy conversion efficiency of DSSCs at low illumination intensity. This would enormously extend the indoor application of DSSCs. The effects of Zn-doping on DSSC performance are interpreted in relation to the obtained material properties and electronic mobility.

Because Zn^{2+} can intercalate into the layered titanate, the dissolution of Zn^{2+} ions into the lattice of the consequent TiO2 products would occur. The ionic radius of Zn^{2+} (74 pm) is larger than that of Ti^{4+} (60 pm). Thus, substituting Zn^{2+} for Ti^{4+} may lead to TiO_2 lattice expansion. The typical Ti K-edge XANES spectra of the H240, TZ04, TZ07 and TZ12 powders are shown in Fig. A2. The A3 peak energy position was 4971.7 eV for H240 and decreased to 4971.4 eV for TZ12. This indicates that the first shell oxygen coordination number of the Ti^{4+} for H240 is more close to 6-fold. Moreover, there is another obvious difference in the intensity ratio of A2/A3, which is an increasing function of the distortion degree in the octahedral TiO_6 unit. The distortion of the Ti^{4+} octahedral symmetry in the anatase structure is stronger in the H240 TiO_2 powder relative to that in the Zn-doped TiO_2 powder.

For doping levels lower than 0.4 at%, the substitution of Zn^{2+} for Ti^{4+}gave rise to an increase in the donor density, with a corresponding negative shift of the Fermi level. However, with further doping with Zn the donor density was remained unchanged while the Fermi level exhibited a substantial negative shift. With Zn-doping, the elevated Fermi level, can increase the slope of downward band bending within the TiO_2 nanoparticles. As indicated in Fig. 2, the number of empty traps (with energy levels between the bottom of conduction band and the quasi-Fermi level) is reduced as a result of the enhanced downward band bending. Because of the decrease in the number of empty trap states, the frequency of the multiple-trapping event can be minimized, leading to higher mobility for electrons in the Zn-doped TiO_2 film. This influence would be especially prominent in a lowintensity illumination situation, in which the probability of a travelling electron to be localized by trap states is great.

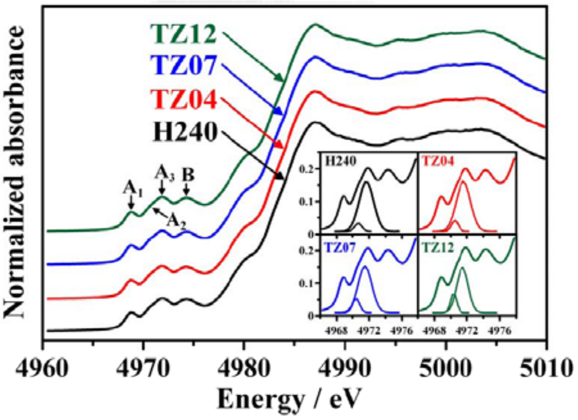

Fig. 1: X-ray absorption near-edge structure spectra of the H240, TZ04, TZ07 and TZ12 TiO_2 nanoparticles. The insets show the A2 and A3 peaks from fitting.

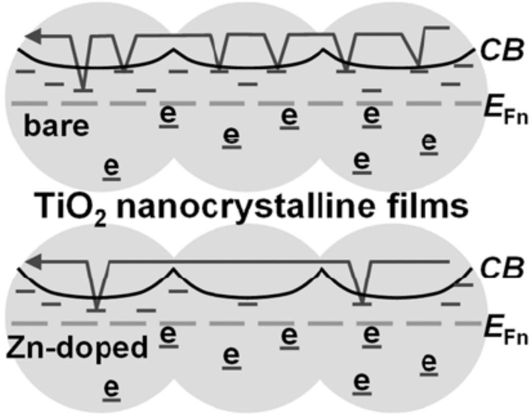

Fig. 2: Schematic illustration showing the trap distribution and the multiple trapping/detrapping process occurring in two types of nanocrystalline TiO_2 films, bare and Zn-doped. The trap states with energy levels situated between the conduction band edge (CB) and quasi-Fermi level (EFn) are empty and available for the electron trapping/detrapping event, while the trap states with their energy levels lower than EFn are occupied with electrons.