Effect of Mixed Structure of Anatase and Rutile on Catalytic Activity of TiO_2 Catalysts

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Charge transfer mechanism of semiconductor photocatalysts was investigated on a mixed crystal of anatase and rutile by electrolumisecence (EL) characteristics in order to clarify optimum fabrication conditions for obtaining active photocatalysts. The mixed crystal films were obtained by oxidation of $TiO(OH)_2 xH_2O$ gel films electro-deposited on Ti metal sheets which allows us to heat-treat them at high temperatures (300-800 ^{o}C) and to prepare a mixed crystal of anatase and rutile with a desired ratio. TiO_2 film composed of anatase and rutile was proved to be

more catalytically active than that composed of anatase alone or rutile alone. This is ascribed to be due to the co-existence of anatase and rutile, where rutile acts as an effective electron scavenger (sacrifice anode) mediating reduction reactions between photogenerated majority carriers (electrons) and protons and/or water in an electrolyte.

The EL band peaked at 840 nm was found to be uniquely observable only for rutile phase and not for anatase phase. This EL band is ascribed to be due to electron transfer from the conduction band to intermediates produced by proton intercalation in the atomic gap existing on rutile surface alone. As a result, rutile/electrolyte interface acts as a sink for excess electrons, the scavenging of which is of vital importance for keeping the catalysts active. In other words, photogenerated holes are quickly consumed both on anatase and rutile surfaces by oxidation reactions with reactants in the electrolyte, leaving photogenerated electrons in the conduction bands of anatase and rutile. Accumulation of negative charges in the conduction bands lower the band bendings, which lower the photocatalytic activity. However, if rutile coexists with anatase, it can accept electrons from anatase, acting as a sacrifice anode because the conduction band edge of rutile is lower than that of anatase, keeping the band bending of anatase up. Furthermore, electrons accumulated in rutile are likely to be easily scavenged from it by reduction reactions with water and/or proton because it contains a lot of atomic gaps which give space for easier inter-/deinter-calation of protons. This is the proposed mechanism why a mixed crystal of anatase and rutile is more catalytically active than anatase alone.