Strategies developed on the modification of titania for visible light response with enhanced interfacial charge transfer process: an overview

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Abstract: The modification of titania by metal / non metal ion doping, coupling with narrow band gap sensitizer, surface fluorination, metal deposition, and together with recent ventures on application of {001} facets of anatase titania for visible light response with enhanced charge carrier separation are briefly overviewed.

Keywords: Titania • Doping with metal / non metal ion • Surface fluorination • Metalization • {001} anatase facet

1. Introduction

Since the photoelectrochemical splitting of water using TiO$_2$ was first reported by Fujishima and Honda in 1972 [1], the application of TiO$_2$ in several fields has drawn significant interest by several research groups. However, the high density of charge carrier recombination and also the large band gap of TiO$_2$ impair its commercial applications. Recently intense research has been devoted to modification of the titania band gap as well as to utilization of the large fraction of solar light with high quantum efficiency for commercial applications. In this regard, main landmark achievements are represented in Scheme 1.

2. Strategies developed to harvest solar light with enhanced separation of charge carriers in titania

The band gap excitation of TiO$_2$ by UV light generates charge carrier pairs with robust redox properties. Those pairs may recombine, become trapped in the metastable surface state or react with electron acceptors / donors adsorbed on the surface of the photocatalyst (Path 1). Doping of metal ions within certain limits prolongs the charge carrier life time and also extends the band gap absorption to the visible region either through d-d transition or interband transition from dopant level to band gap states of TiO$_2$ (Path 2) [2a]. Metal ion doped titania prepared by applying ion-engineering techniques such as ion-implantation and an Radio Frequency magnetron sputtering deposition method showed high efficiency for water splitting under visible light [2b]. Although, reports on enhanced activity of metal ion doped TiO$_2$ compared to the benchmark photocatalyst Degussa P25 is widely reported [2c], the thermal instability as well as increased recombination due to metal ion inclusions limits its scope [2d].

Asahi et al. reported the TiO$_2$-N$_2$ films prepared by sputtering the TiO$_2$ target in a N$_2$ (40%) / Ar gas mixture for the degradation of methylene blue and gaseous acetaldehyde under UV / Visible light [3a], while Khan et al. reported the water splitting using rutile TiO$_2$ doped with carbon as substitutional impurity [3b]. In contrast to the metal ion doped TiO$_2$, wherein metal ion forms a localized electronic level, the p orbital of substituted non metal atom hybridize with O 2p orbital resulting in visible light response. Although it is recently argued that in the case of doped titania visible light response mainly originates from color centers [3c]. Non metal ion doping into anatase titania lowers the oxidation power of holes.

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