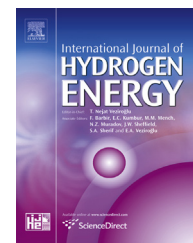


Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/hydro

Enhancing photocatalytic properties of rutile TiO₂ by codoping with N and metals – Ab initio study

J. Belošević-Čavor^{a,*}, K. Batalović^a, V. Koteski^a, J. Radaković^a,
C.M. Rangel^b

^a Institute of Nuclear Sciences Vinča, University of Belgrade, P.O. Box 522, 11001 Belgrade, Serbia

^b LNEG, National Laboratory for Energy and Geology, Paço do Lumiar 22, 1649-038 Lisbon, Portugal

ARTICLE INFO

Article history:

Received 1 April 2015

Received in revised form

23 May 2015

Accepted 1 June 2015

Available online 22 June 2015

Keywords:

N-metal codoped rutile TiO₂

Photocatalytic efficiency

First principles calculations

ABSTRACT

Substitutional N to O and M to Ti (M = Pt, V, Sb) codoped rutile TiO₂ was investigated using density functional theory (DFT) based calculations with both standard and hybrid exchange-correlation functionals. The band gaps calculated using generalized gradient approximation (GGA) exhibited narrowing compared to the pure rutile TiO₂ in all the investigated cases. In contrast, the results obtained with hybrid exchange-correlation functional showed that there was no band gap narrowing, but doping induced localized states within the band gap just above the valence band, as well as below the conduction band for Pt doped TiO₂. The presence of broad intermediate states (IS) in the band gap could enhance visible light absorption through a two step optical transition from the valence to the conduction band via the IS and at the same time lower recombination of the photo-generated charges.

Copyright © 2015, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

The most efficient way of hydrogen production using solar energy is water splitting induced by solar light. In order to achieve it, a photo-semiconductor capable of absorbing solar energy efficiently is needed. Efficient photocatalysts should satisfy several conditions: suitable band gap (about 2–2.2 eV) for visible light absorption and appropriate band edge potentials for water splitting, capability to separate excited electrons and holes, minimal energy losses during charge transport, chemical stability to corrosion, suitable electron transfer properties from photocatalysts' surface to water and low cost [1,2]. However the applicability of semiconductor

photocatalyst is, without any doubt, primarily determined by its electronic structure.

Titanium dioxide TiO₂, in both rutile and anatase form, is one of the most promising photocatalysts. However, the wide energy gaps of pure TiO₂ phases allow efficient absorption of only ultraviolet light and are not suitable for efficient use of solar energy. In this sense, an extensive experimental [3,4] and theoretical [5–14] work has been carried out in order to shift the TiO₂ absorption edge from the UV to the visible-light region and thus increase its efficiency for solar-driven photocatalysis. For achieving that purpose mostly doping with transition metals was used [15–22]. However, the transition metals as dopants can increase the number of carrier-recombination centers and thus reduce the carrier mobility,

* Corresponding author. Tel.: +381 11 3408 549; fax: +381 11 3408 681.

E-mail address: cjeca@vinca.rs (J. Belošević-Čavor).

<http://dx.doi.org/10.1016/j.ijhydene.2015.06.001>

0360-3199/Copyright © 2015, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.