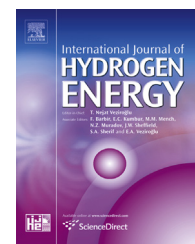


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# Enhancing photocatalytic properties of rutile TiO<sub>2</sub> by codoping with N and metals – Ab initio study

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## ABSTRACT

Substitutional N to O and M to Ti (M = Pt, V, Sb) codoped rutile TiO<sub>2</sub> 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 TiO<sub>2</sub> 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 TiO<sub>2</sub>. 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.

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## 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 TiO<sub>2</sub>, in both rutile and anatase form, is one of the most promising photocatalysts. However, the wide energy gaps of pure TiO<sub>2</sub> 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 TiO<sub>2</sub> 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,

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