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The electronic structure, optical absorption and photocatalytic water splitting of (Fe + Ni)-codoped TiO₂: A DFT + U study

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ARTICLE INFO

Article history:

Received 19 December 2015

Received in revised form

23 May 2016

Accepted 7 June 2016

Available online xxx

Keywords:

TiO₂

Codoping

Photocatalytic water splitting for hydrogen generation

Density functional theory

ABSTRACT

The electronic and optical properties of Fe or/and Ni (co)doped anatase and rutile TiO₂ were investigated using the spin-polarized density functional theory. Our calculated results indicate that the synergistic effect of (Fe + Ni) codoping can lead to a band gap narrowing and the hybridized states of Fe 3d and Ni 3d appearing in the forbidden gap, which enhances greatly the optical absorption of TiO₂ nanomaterials from the ultraviolet-light to the infrared-light region and reduces the recombination of photogenerated electron–hole pairs. In particular, (Fe + Ni) codoping can improve greatly the infrared-light absorption of TiO₂ nanomaterials. Furthermore, the researches of electronegativity show that (Fe + Ni)-codoped TiO₂ system has a stronger redox power for hydrogen generation by photocatalytic water splitting compared with pure, Fe-doped, and Ni-doped TiO₂ systems. These results lead to an outstanding solar energy photocatalytic water splitting for hydrogen generation in (Fe + Ni)-codoped TiO₂ photocatalyst.

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Introduction

Finding sufficient supplies of clean energy for the future is one of society's most daunting challenges due to the limited supply of traditional energy (coal and oil) and their detrimental effects on the global climate. Solar energy is considered to be the most important candidate because it is abundant, clean and renewable. The photoelectrochemical cell splits water

into hydrogen and oxygen, so as to convert the solar energy into chemical energy, and has attracted increasingly attention since the discovery of water splitting property of titania (TiO₂) electrodes under ultraviolet (UV) light illumination [1] due to the versatile applications of hydrogen and oxygen gases. In order to relieve the energy crises, environment pollution and global warming, utilization of solar energy using photocatalytic water splitting for hydrogen generation of TiO₂ nanomaterial has been extensively studied [2–8]. However,

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<http://dx.doi.org/10.1016/j.ijhydene.2016.06.077>

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the energy conversion efficiency of TiO₂ is low in photocatalytic water splitting. This is mainly because TiO₂ has a wide band gap (3.2 eV for anatase [9] and 3.0 eV for rutile [10]); thus, TiO₂ absorbs only a small portion of the solar spectrum in the UV-light ($\lambda < 400$ nm) region. It is well known that to achieve high efficiency, the desirable photocatalyst should have a band gap around 2.0 eV and the positions of its band edges must be matched with the redox potentials of water [11]. Therefore, reducing the band gap of TiO₂ to make it photosensitive to visible-light and placing the band edges of TiO₂ at proper potential levels to enhance its redox power has become two important goals in photocatalytic water splitting for hydrogen generation.

In recent years, considerable efforts have been devoted to modifying the electronic structure of TiO₂ materials, one of the effective strategies is doping TiO₂ with different cations and anions to reduce its band gap and improve its visible-light absorption [12–19]. For instance, Yang et al. studied systematically the nitrogen concentration influence on N-doped anatase TiO₂ [13]. The results indicate that some localized N 2p states are formed above the valence band in N-doped anatase TiO₂ at lower doping levels, which enhance the optical absorption of visible-light region. And the band gap has little further narrowing compared with that at lower doping levels when the doping level rises. Chen et al. investigated the electronic and photocatalytic properties of Fe-doped TiO₂ anatase (101) surfaces by a spin-polarized density functional theory (DFT) [15]. The calculated results of density of states show a band gap narrowing from 2.8 to 1.9 eV comparing with the pure TiO₂ surface due to the synergistic effects of surface Fe impurities with O vacancies, and finding that the influence of Fe impurities on the electronic structure of the system is localized. Liu et al. reported a simple but efficient way to synthesize black Ni-doped TiO₂ photoanodes for photoelectrochemical water-splitting [19], which indicates that the black Ni-doped TiO₂ photoanodes exhibit an excellent and stable photocatalytic activity compared to undoped TiO₂ photoanode. Some researches indicate that different elements codoping into TiO₂ can further narrow its band gap and enhance its photocatalytic activity [20–29]. For example, Shi et al. reported the photocatalytic activity of Fe³⁺ and Ho³⁺ ions codoping TiO₂ [21]. The results show the photocatalytic activity of TiO₂ codoped with Fe³⁺ and Ho³⁺ ions is markedly improved due to the cooperative actions of the two dopants. Long et al. investigated systematically the influence on electronic properties of anatase TiO₂ of codoping by N and Si using Heyd–Scuseria–Ernzerhof (HSE06) hybrid density functional theory calculations [23]. Jia et al. studied the microscopic mechanism for band gap narrowing and the origin of the enhanced visible-light photocatalytic activity in N/S-codoped anatase TiO₂ [25]. Dashora et al. investigated the electronic and optical properties of Cu–N-codoped anatase TiO₂ by the first-principles calculations and experiments [27], the results indicate that strong hybridization between Cu 3d and N 2p orbitals above the valence band leads to the formation of an isolated intermediate band (IB) deep in the band gap of pure TiO₂. This IB is responsible for high visible-light absorption through a two-step optical transition between valence and conduction bands via the IB, and the presence of broad IB and the absence of dopant energy levels close to the conduction

band minimum in (Cu + 2N)-codoped TiO₂ qualify it to be an efficient material for photocatalytic water splitting. Belošević–Čavor et al. studied the electronic structures and photocatalytic properties of N and various metal dopants codoped rutile TiO₂ using DFT [29]. The theoretical results show that the presence of broad intermediate states in the band gap can enhance visible-light absorption through a two step optical transition from the valence band to the conduction band via the intermediate states and at the same time lower recombination of the photo-generated charges. These results indicate that different elements codoping is one of the most effective approaches to extend the absorption edge to the visible-light range and improve the photocatalytic activity in TiO₂.

Recently, Sun et al. prepared successfully the (Fe + Ni)-codoped TiO₂ nanoparticles by alcohol thermal method with tetrabutyl titanate as the Ti source [30]. The experimental results indicate that the prepared (Fe + Ni)-codoped TiO₂ photocatalyst has a redshift of the optical absorption edge and a higher photocatalytic activity for hydrogen generation by water splitting under visible-light irradiation. However, to the best of our knowledge, there has been few reports regarding the physical and chemical mechanism of photocatalytic water splitting for hydrogen generation of (Fe + Ni)-codoped TiO₂, especially the essential reasons of causing various optical absorption and redox potential with Fe and Ni elements codoping TiO₂ materials. To address these question, in this work, we studied systematically the synergistic effect of (Fe + Ni) codoping TiO₂ on the mechanism of the redshift of optical absorption edge and the origin of enhanced visible-light photocatalytic activity for hydrogen generation by water splitting using the spin-polarized DFT calculations. In addition, to probe the redox power of Fe or/and Ni (co)doping TiO₂ photocatalyst, the role of electronegativity of Fe and Ni (co)doping TiO₂ in the photocatalytic water splitting for hydrogen generation is elucidated in our work. This investigation will provide new insight into understanding the physical and chemical mechanism of enhanced visible-light photocatalytic activity for hydrogen generation by water splitting in (Fe + Ni)-codoped TiO₂, and designing new photocatalytic materials with required electronic property.

Calculational models and details

To simulate the different (co)doping patterns of Fe and Ni elements in anatase and rutile TiO₂, we constructed Fe and Ni atoms substituting lattice atoms (O and Ti atoms) in the relaxed (2 × 2 × 1) anatase and relaxed (2 × 2 × 2) rutile TiO₂ supercells (containing 16 Ti atoms and 32 O atoms). A variety of possible Fe or/and Ni (co)doping anatase and rutile TiO₂ configurations were considered by replacing O atom or Ti atom in the lattice with a Fe and a Ni atom. In the monodoping TiO₂ models, one impurity atom (Fe or Ni) in the forms of a substitutional atom to the O atom (Fe@O or Ni@O) and a substitutional atom to the Ti atom (Fe@Ti or Ni@Ti) were doped into the supercells of TiO₂, respectively. But in the (Fe + Ni)-codoped TiO₂ models, one Fe atom and one Ni atom were simultaneously doped into the supercell of TiO₂, which resulted in four different kinds of (Fe + Ni)-codoped TiO₂

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