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Synergetic interplay between metal (Pt) and nonmetal (C) species in codoped TiO_2: A DFT+U study

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ABSTRACT

The structural, energetic, magnetic and electronic properties of Pt–C-doped and Pt/C-codoped TiO_2 have been studied using first-principle calculations to elucidate the effect of the metal–nonmetal interactions.

Compared with other non-metals, C-doping induces the formation of complex structures on titania. From the analysis of the electronic structures of the C-doping system, band gap narrowing as well as the formation of localized gap states are observed in it. The calculated results are in agreement with the experimental absorptions observed in the UV–visible diffuse reflectance spectroscopy spectra. Based on our results, the main findings relating to Pt/C codoping are the formation of highly symmetric coordination-like compounds and the formation of impurity states in the band gap that could be propitious for the separation of photoexcited electron–hole pairs. Is especially remarkable the case of Pt/C@Ti-codoped TiO_2 which could be the most effective for the redox reaction of H_2O to produce H_2 and O_2 because it presents the greatest narrowing of the band gap, the lower shift of the conduction band and it is the only one that favorably modifies the position of valence band. All are necessary conditions for the reaction mentioned.

1. Introduction

The titania (TiO_2) has its own name not only for its technological but also for its catalytic applications, including WGS reaction [1] and photocatalysis among others, in its role as a photocatalyst in remedial reactions of environmental contaminants [2,3]. It has attracted interest in the study of possible modifications thereof, in order to optimize the absorption of solar radiation by changing its wide band gap (BG), its potential redox and the half-life of charge carriers generated in the titania activation.

In order to access the conduction band (CB), the electrons in the valence band (VB) need radiation of about 380 nm or less. In both polymorph systems, anatase (A) and rutile (R), the VB is located deep in energy generating holes with high oxidative power. However, the location of the CB bottom is close to reducing the potential of hydrogen [4], indicating weak reduction potentials. This effect is more pronounced in rutile than in anatase. On account of these differences in the position of the CB and indirect BG, anatase exhibits higher photoactivity [5].

Therefore, enhancing the oxide-reductive properties of titania (A and R) under energies corresponding to the visible solar spectrum, is a prerequisite for improving their activity and this implies a reduction in the value of their BG. Both, excited electrons from the valence band to the conduction band and holes generated in the process can migrate to the surface and react with electron donors or acceptors, respectively, or recombine releasing the absorbed energy. It is desirable that the titania modification generates not only a reduction in the required activation energy but also a decline in the recombination of the generated charges. Some studies have been published showing that the doping of the system with anionic species such as nitrogen, carbon and sulfur can potentially form new impurity levels closest to the valence band, reducing the width of the bandgap for maximum efficiency [6]. In particular, the C-doping has proved to be five times more effective than N-doping in the degradation of 4-chlorophenol with artificial light ($\lambda > 455$ nm) [7]. But nevertheless, despite recognition of the advantages of C-doping in the photocatalytic activity of titania, the understanding of electronic mechanisms involved in the process is still very limited.

Moreover, many studies of doped titania have been performed either in the anatase phase or in crystals which have different proportions of the most abundant polymorphs. Specifically, there is scant literature where the presence of C dopant in the rutile structure is examined, despite the well-known phase transformation from anatase to rutile at high temperatures. Certain technological

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processes are performed at temperatures belonging to the range of the transition temperature ranging between 823 K and 953 K [8]. Furthermore, Shen et al. found that the transformation from anatase to rutile occurs when heating a sample doped with C at temperatures near 623 K for a long time assuming that the C-doping could also modify the phase transition temperature of the system [9].

In relation to experimental studies, the preparation methods and precursors used as reagents in obtaining samples have shown significant influence on both polymorphs. The C impurities on doped systems were identified, using X-ray photoelectron spectroscopy (XPS), as carbides, carbonates and carboxyls depending on the preparation method [10]. The presence and concentration of vacancies, the distances between them and the doping atoms, the purity of the sample, the degree of crystallinity, grain size and temperature, pressure and working atmosphere, are parameters to be considered in the experimental work [6]. In particular, photo-reactivity is critically dependent on the defects in the material. The differences observed in experimental studies imply that the understanding of these types of structures in each case requires a rigorous theoretical study. The greatest difficulty in analyzing the results published in the literature arises from the different forms of theoretical representation used to model the system as well as the computational codes, dopant concentrations and the internal distances between atoms of impurities within the crystal [11].

With respect to the metal-doped, several studies show that noble metals such as Pt are usually deposited on TiO_2 as co-catalyst but some metal atoms diffuse into the bulk during sample preparation. However, there are few studies on Pt as a doping ion within the crystal. It has been shown that the Pt ion metal as dopant exhibits unique characteristics for the degradation of 4-chlorophenol and dicloacetate [12]. Furthermore, it has been experimentally observed that Pt impregnation in mesoporous nanocrystals of N-doped titania improves photocatalytic H_2 production considerably [13]. Moreover, recent studies on materials based on C-doped titania modified with Pt have shown an activity six times higher in the degradation of toluene in air compared to the activity observed in systems without the addition of Pt. The activity increment could be attributed to activation by visible light and the improvement in mobility processes and separation of charge carriers [14]. Other experimental results support that the mixed doping with transition metals and nonmetals greatly enhances the inhibition of recombination of charge carriers. Therefore, it is necessary to know accurately which ones are the contributions that each doping atom provides to the system. The accepted hypothesis is that the bands partially occupied close to the VB, resulting from the presence of nonmetal impurities, act as recombination centers (electrons of the partially occupied impurities states would annihilate the holes generated by the radiation absorbed) or as mobility reduction centers of charge carriers (the states of the metal impurities, near the CB, would immobilize the excited electrons) [15].

In this paper the structural, magnetic and electronic properties of C-doped titania in anatase and rutile structures are investigated considering different dopant sites, concentrations and carbon oxidation states. With the aim to obtain insight into the metal–nonmetal codoping effects, for example, by introducing additives of 5*d* and 2*p* elements we have performed a careful theoretical analysis of the energetic, structural and electronic properties of Pt/C-codoped anatase TiO_2. The innovation of this work is to provide a theoretical study of structural and electronic properties of TiO_2 systems codoped not studied thus far and as a potential trigger of new experimental studies to confirm our findings. The modification of properties in a controlled manner encourages the efficiency of the ab initio calculations.

2. Theoretical framework

Total energy DFT calculations were performed using the Vienna Ab-Initio Simulation Package (VASP) code [16] and the projector augmented-wave method (PAW) developed by Blöch to describe the ion–electron interactions [17]. We adopted the generalized gradient approximation for the exchange–correlation energy due to Perdew and Wang (GGA-PW91) [18]. The basis of plane waves were generated considering 4 valence electrons for Ti ($3d^3 4s^1$), 6 valence electrons for O ($2s^2 p^4$), 10 electrons for Pt ($5d^9 6s^1$) and 4 electrons for C ($2s^2 p^2$). The limit considered for the kinetic energy of expansion of plane waves was 450 eV. The Brillouin zone integration was performed on well-converged Monkhorst–Pack *k*-point meshes. For the *k*-point integration, we used $10 \times 10 \times 10$ mesh for the $(1 \times 1 \times 1)$ unit cells representation employed in systems with high concentrations of impurities (Fig. 1a), $3 \times 3 \times 3$ mesh for the $(3 \times 3 \times 1)$ anatase supercell of 108 atoms in order to represent the anatase doped system with low concentrations of impurities (Fig. 1b); $5 \times 5 \times 5$ mesh for C-doped rutile represented by a $(2 \times 2 \times 2)$ supercell (Fig. 1d) of 48 atoms [19]. The criterion for the self-consistent convergence of the total energy was 0.1 meV and the cell parameters were optimized using forces smaller than 20 meV/Å as conversion criteria. The value of Hubbard coefficient for corrections of Coulomb interactions of the Ti *d* electrons was optimized to a value of 8 eV. In this work, we use the Dudarev's approach [20] implemented in the Vienna Ab-Initio Simulation Package (VASP) through careful selection of U, achieving excellent matches with the experimental band gap and bulk modulus measured for the systems investigated. A research performed by our group, has just been published using the same value of U [21]. All calculations were performed at the spin polarized level.

For each optimized structure, both on rutile and anatase, the density of states (DOS) was calculated to obtain the corresponding electronic structure and band gap value (BG). The study was completed evaluating the corresponding magnetic moments per atom (μ in μ_B) and Bader charges [22] were calculated to conclude the analysis. The interatomic distances, angles and cell parameters were determined and the isosurfaces were obtained using VESTA [23].

3. Results and discussion

The main objective of this work is the analysis of the effect of Pt/C-codoping in titania. Moreover, in order to complete the analysis of carbon doping in TiO_2 we compare our theoretical results with published experimental ones in a special section.

Doping nature has extensive implications in the crystalline solid configuration and thus in their optical, structural and magnetic properties. The distortion of the symmetry with respect to the stoichiometric solid has not only structural, but also catalytic inferences accompanied by changes in electronic charge distribution and in its photocatalytic oxidation–reduction behavior. The degree of geometric distortion in the case of C addition in titania is largely dependent on the position of the impurity in the crystal structure which in turn determines the strongly anionic or cationic behavior thereof. The formation of CO_2 and CO_3 type structures within the crystal are specific to the unique nature of C characteristics compared to other nonmetals studied.

3.1. Carbon doping

In this section the results obtained for carbon impurities located in different sites and at different concentrations on both doped polymorphs, are discussed. The notation used is the following: first, the titania polymorphic type (A, R), then the type of site