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Theoretical study of the rutile based semiconductor with visible-light responsive photocatalytic activity for water splitting

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ABSTRACT

The cluster expansion formalism combined with the accurate first-principles calculations were performed to investigate the stabilities, the electronic structures and the optical absorption of the rutile based semiconductor $\text{TiPt}_x\text{O}_{16}$. Our comprehensive calculations have predicted that $\text{TiPt}_7\text{O}_{16}$ is the most stable structure among the hundreds of the configurations of Pt substituted rutile TiO_2 ($\text{Ti}_{1-x}\text{Pt}_x\text{O}_2$ (R), $x = 0-1$). More importantly, the accurate HSE06 calculations indicate that $\text{TiPt}_7\text{O}_{16}$ is a potential visible-light responsive photocatalyst with the band gap of 1.70 eV. In addition, the Pt-terminated (010) and Ti & Pt-terminated (011) surfaces are suitable for catalyzing the overall water splitting, due to their band edges span over the required redox potential.

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Introduction

In 1972, Fujishima and Honda firstly invented the TiO_2 based photocatalytic water splitting system [1], leading the water splitting photocatalysis to become an extremely attractive research field, paving a promising road to attain energy from the sunlight. Although lots of oxide semiconductors exhibit a good performance as photocatalyst in water-splitting [2–4], TiO_2 has been thought of as a preferential material because of its excellent catalytic activities, as well as the advantages of nontoxic, water insoluble, long-term stable and anti-photocorrosive.

As the development of photocatalysis research, the water-splitting mechanism has been quite well illustrated. The electron-hole pairs generated at the initial stage by absorbing photons when the material irradiated under sunlight, and then the electrons transfer to the conduction band from the valence band, leaving the holes in the valence band. Subsequently, the photo-induced electrons and holes participate in the hydrogen reduction and oxygen oxidation reactions to generate H_2 and O_2 : $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$; $\text{H}_2\text{O} + 2\text{h}^+ \rightarrow (1/2)\text{O}_2 + 2\text{H}^+$, respectively. In principle, the occurrence of the photocatalytic water splitting reaction must meet some requirements: (1) the band gap of the semiconductor must be larger than the free energy of water

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splitting of 1.23 eV [5]; (2) the conduction band minimum (CBM) must be higher than the H^+/H_2 reduction potential of -4.44 eV (pH = 0) and the valence band maximum (VBM) energy must be lower than the O_2/H_2O oxidation potential of -5.67 eV (pH = 0) [3,6,7]. As a promising photocatalytic water splitting candidate, TiO_2 matches the two conditions well. However, a serious and unavoidable weakness is that only about 3%–5% of the solar spectrum can be absorbed for photocatalytic reaction due to the wide band gap [3,8,9]. In other words, the solar energy conversion efficiency of TiO_2 is rather limited.

Therefore, improving the photocatalytic performance of TiO_2 is an urgent task for the photocatalysis research. Many experimental and theoretical efforts [10–13] were made to modify its electronic structures to improve its optical absorption of visible light. Alien ions doping/codoping is a popular and effective way to tune the band gap of TiO_2 . Lots of transition metal elements (Fe, Co, Cu, Nb, Pt, etc.) have been used as the dopants to enhance the photocatalytic activity of TiO_2 under the visible-light [14–16,21,22] owing to the additionally occupied doping states created in the band gap of TiO_2 . Non-metal species (e.g., N) [10,17–20] doping can generate new states overlapping with the valence band edge of TiO_2 to shift the fermi level upwards to narrow the band gap. It has been demonstrated that co-doping Cr-N pair into TiO_2 ensures the appearance of the tunable intermediate bands to remarkably narrow the band gap of the host materials [21,22]. However, an overview of the reported results indicates that the solubility of dopants in the binary oxide semiconductors is rather limited. In addition, the dilute dopants usually generate local impurity energy levels in the band gap and create recombination center for photo-generated carriers, leading to ineffective promotion of the photo-electrochemical energy conversion. It is quite critical that the introduction of the alien atoms can narrow the band gap of the semiconductor, and maintain the highly dispersive characteristics of the energy bands at CBM and VBM, as well as the suitable band edge positions which still stride over the redox potential of water splitting.

Motivated by the catalytic activity of Pt for water dissociation [23], as well as the matched ionic radius of six-coordinated Pt^{4+} with that of Ti^{4+} , we attempt to employ a combination of first-principles calculations with the cluster expansion (CE) approach [24–27] to investigate the possibility and the concentration of introducing Pt into rutile TiO_2 (R) on the Ti sites, followed by the calculations of the electronic structures to evaluate the photocatalytic performance of the structure(s) of Pt-doped TiO_2 (R).

Computational methods

The atoms configuration of the cation sublattice sites in the $Ti_{1-x}Pt_xO_2$ (R) system that were appointed by a spin-like occupation varied to the element species, e.g. $\sigma_i = +1$ and -1 were imposed to Pt and Ti on the cation sites, respectively. Therefore, the occupation variables collection of $\vec{\sigma} = \{\sigma_1, \dots, \sigma_2, \dots, \sigma_M\}$ uniquely are constructed by the Ti and Pt arrangement. Within the cluster expansion, the configurational energy E is expressed as the follow polynomial,

$$E(\vec{\sigma}) = V_o + \sum_i V_i \sigma_i + \sum_{ij} V_{ij} \sigma_i \sigma_j + \sum_{ijk} V_{ijk} \sigma_i \sigma_j \sigma_k + \dots \quad (1)$$

where the coefficients V_i , V_{ij} , V_{ijk} , ..., are the effective cluster interactions (ECIs) for pairs, triplets and quadruplets, etc.. The values of ECI were determined by fitting equation (1) to the first-principles total energies of the selected configurations using a root mean square method. In practice, the polynomials of equation (1) should be truncated to qualify the precision and physical features of the cluster expansion [24,28,29]. The set of optimal ECIs can be generated by the weighted cross-validation (CV) score [24,28]. The effective Hamiltonian was determined from the set of ECIs by using a genetic algorithm [30].

The structure optimization and total energies calculations of the selected configurations were performed using the Vienna *Ab Initio* Simulation Package (VASP). The Projector Augmented Wave (PAW) potentials [31] were used for the core electron treatment. The generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) functional was applied to describe the electron exchange correlation interactions [32]. A soft oxygen pseudopotential with valence configuration $2s^2 2p^4$ and default cutoff energy of 282.84 eV was used. Therefore, the cutoff energy for the plane-wave basis was set to 350 eV for all spin-polarized first-principles calculations. Suitable K-point meshes with a minimum number of 46 KPOINTS were sampled based on the Monkhorst-Pack scheme [33] for the full relaxation of the atom positions and the lattice vectors of the configurations to ensure the force on each atom converged to within 0.02 eV/Å.

In order to overcome the deficiency of describing the exchange-correlation (XC) energy in the standard first-principles calculations, the screened Heyd–Scuseria–Ernzerhof (HSE06) hybrid functional [34–36] calculations were performed for the secondary geometry optimization and investigation of the electronic structures of the ground state(s) generated by the cluster expansion prediction. The exact XC was described by 25% Hartree–Fock (HF) exchange and 75% PBE contributions, which produced accurate lattice constants and band gaps of rutile and anatase TiO_2 as compared with the experimental and other theoretical values [37,38].

Results and discussion

Since the ionic radius of Pt^{4+} matches well with that of the counterpart Ti^{4+} , it is reasonable to expect that Pt can substitute the Ti atoms in TiO_2 (R), and eventually lead to the formation of PtO_2 (R) to the upper limit. The rutile phase PtO_2 (R) is not the most stable structure of PtO_2 , but this structure actually has been prepared experimentally at high pressure [39]. Furthermore, theoretical study on the physical properties [40] and electrochemical catalytic activities [41] of the rutile-type PtO_2 were performed recently. Indeed, our testing calculations of Pt substitutionally doped TiO_2 (R) yields the negative formation energies, whereas the interstitial doping results in the positive values. The initial results thus prompt us to carry out a cluster expansion to gauge the extent to

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