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Roles of Cu concentration in the photocatalytic activities of Cu-doped TiO_2 from GGA+U calculations

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ABSTRACT

First-principles GGA+U calculations are performed on the electronic structure of Cu-doped anatase TiO_2 with various Cu concentrations. The results show that the incorporation of Cu into TiO_2 gives rise to a perturbation of electronic structure. The most remarkable feature is the appearance of metal-induced gap states, resulting in the band gap narrowing of host TiO_2. The band gaps reduce with the increase of Cu concentration. Both the positions of valence band maximum and conduction band minimum depend on Cu concentration, which indicates that there should be an optimal Cu concentration to achieve high H_2 generation efficiency.

1. Introduction

Owing to its many advantages, TiO_2 is considered as one of the most promising photocatalysts for hydrogen generation through photoelectrochemical (PEC) water splitting [1–4]. However, due to its large band gaps ($\Delta E_g = 3.0$ eV for rutile and $\Delta E_g = 3.2$ eV for anatase), only a very small portion of solar spectrum can be used for PEC water splitting. This makes the narrowing of band gaps necessary. Two strategies have been used extensively for band gap narrowing: TiO_2-based oxide heterostructures and TiO_2 doped with foreign elements [5,6]. In fact, great efforts have been made to narrow the band gap of TiO_2 by mono-doping with cation or anion, or by co-doping with both cation and anion. Researchers have found many potential doped TiO_2 structures with appropriate band gaps and band edges [7–10].

The doping transition metals (TM) into TiO_2 have been extensively investigated both experimentally and theoretically. The common feature of these doped TiO_2 structures is that a small portion of d energy levels of TMs enter into the forbidden bands of TiO_2 host. This reduces the band gap and thus extends optical absorption into the longer wavelength regions [11,12]. The main differences among these doped TiO_2 lie in the specific locations of these dopant energy levels, and this is due to the energy differences of the d electrons of TMs [13]. These dopant energy levels are either slightly higher than intrinsic valence bands (VB) or slightly lower than intrinsic conduction bands (CB) for the p-type or n-type semiconductors. These divide the forbidden gaps of the TiO_2 host into sub-gaps, which act as stepping stones to relay valence electrons to the conduction bands via multi-photon excitations. The aforementioned results have made important contributions in understanding the mechanism of the enhanced photocatalytic activities of TM-doped TiO_2. This helps one to design better photocatalysts. It is worth pointing out that first-principles calculations, based on density functional theory (DFT), play a more and more important role in exploring both the atomic and the bonding behaviors of the dopants [14–16].

Among the dopants investigated, Cu is important because it has high electronic conductivity, and is cheap and abundant in Earth. Cu-doped TiO_2 have been demonstrated to have high photocatalytic efficiency. This is mainly due to the fact that Cu doping can reduce the band gap of TiO_2 to an appropriate value for hydrogen generation through PEC water splitting [17–23]. However, the microscopic understanding of the enhanced photocatalytic activities of Cu-doped TiO_2 is limited, as compared to the investigations of other TM-doped TiO_2. Almost no systematic theoretical exploration has been conducted on this material system [24–26]. In addition, from the available theoretical literature on TM-doped TiO_2, we find that the great majority of works only consider how a fixed concentration of TM dopant reduces the band gaps of TiO_2. Few of these investigations pay attention to the photocatalytic mechanisms of TM-doped TiO_2 with various concentrations. Experimental results demonstrate that Cu concentration has a significant influence on hydrogen generation, and that the optimal

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Cu concentration could be existed [27]. In addition, many conventional DFT methods underestimate the intrinsic band gap of TiO_2, owing to the well-known limitation in its treatment of the electron self-interaction. Some advanced DFT frameworks such as DFT with a Hubbard parameter U (DFT+U) and hybrid DFT are very successful in reproducing the experimental band gaps of TiO_2 [7]. For a complex system, from the computation efficiency point of view, DFT+U methods are appropriate. They are extensively used not only in the transition-metal oxide, but also in many other materials with f electrons [28].

In this paper, we conduct systematic first-principles GGA (Generalized Gradient Approximation)+U calculations on how Cu concentration influences the electronic-structure and optical properties of Cu-doped anatase TiO_2. Our results indicate that Cu is an appropriate dopant and that there exist an optimal Cu concentration for highly efficient PEC water splitting.

2. Computational details

TiO_2 has three well-known crystal polymorphs, i.e., anatase, rutile, and brookite. Particularly, tetragonal-structure anatase TiO_2 has been extensively studied due to its photocatalytic activities and demonstrated effectiveness in hydrogen generation. Thus, we focus on the anatase TiO_2. In order to investigate the influences of Cu concentration on the electronic structure of TiO_2, we construct a $2 \times 2 \times 2$ supercell containing 32 Ti and 64 O atoms. One to four Cu atoms are substituted for Ti atoms to form the doped calculation configurations, as shown in Fig. 1, corresponding to the Cu atomic percentage (at%) or weight percentage (wt%) of 1.04 at%, 2.08 at%, 3.16 at%, 4.16 at% or 2.48 wt%, 4.94 wt%, 7.36 wt%, 9.76 wt%, respectively. It should be noted that the number of possible lattice arrangements of the Cu atoms greatly increases when Cu concentration increases [29]. Therefore, it is extremely difficult to consider all atomic configurations. Some experimental and theoretical results show that TM atoms exhibit a weak trend of clustering. In addition, interstitial and oxygen sites are not preferable to accommodating Cu and other TMs [25]. Therefore, we concentrate on the atomic configurations with clustered Cu atoms. We also calculate some atomic configurations with isolated Cu atoms for comparison.

All of the calculations are carried out by using CASTEP code, with a plane wave basis set for expansion of effective single particle Kohn–Sham energy [30]. Valence states in the ultrasoft pseudopotentials are Ti [Ne] $3s^2 3p^6 3d^2 4s^2$, Cu [Ar] $3d^{10} 4s^1$, and O [He] $2s^2 2p^4$, respectively. A cut-off kinetic energy, 400 eV, is used for plane wave expansions in the reciprocal space. Energy calculations in the first irreducible Brillouin zone are performed using a special k point sampling methods of Monkhorst–Pack scheme and set as $4 \times 4 \times 2$. The tolerances for the geometry optimization are selected as the difference in total energy within 1.0×10^{-5} eV/atom, the maximum ionic Hellmann–Feynman force within 0.03 eV/Å, the maximum ionic displacement within 1.0×10^{-3} Å and the maximum stress within 0.05 GPa, respectively. The electronic self-consistent field (SCF) loop is repeated until the energy difference between the successive loops becomes less than 1.0×10^{-6} eV/atom. The recently improved PBE-WC GGA exchange-correlation potential [31,32] is adopted throughout the calculations with considering the spin-polarized effects.

It is well known that the conventional DFT calculations cannot correctly describe the ground-state of the materials containing open d and f shells, because of their strong on-site Coulomb interactions. Among the methods for treating the strongly-correlated electrons, DFT+U has been widely accepted and proved to be able to describe the behaviors of d electrons in TMs [33,34]. We apply the U correction on both Ti 3d and Cu 3d electrons in order to take account of their strongly-correlated effects. Generally, U corrections to the host Ti 3d electrons and to the dopant Cu 3d electrons are mainly used to open up the band gap and to obtain the reasonable dopant energy levels. Previous works have recommended a variety of values for U in TiO_2 (2.5–10 eV) depending on the properties fitted and the theoretical frameworks of the codes [35]. In the present calculations, optimization of U is mainly performed on the relationship of the band gaps vs U for both TiO_2 and CuO. As shown in Fig. 2, the band gaps of TiO_2 and CuO at $U=7.5$ eV are calculated to be 3.22 eV and 1.20 eV, respectively, which agree well with other experimental and theoretical values [36,37].

3. Results and discussion

The full-relaxation results show that the equilibrium lattice parameters for TiO_2 are $a=b=3.78$ Å, $c=9.54$ Å, which are in good agreement with the experimental and theoretical results. Then, we use the relaxed structure for the construction and relaxation of Cu-doped TiO_2. Generally, the crystal symmetry is preserved and the volume increases slightly with the increase in Cu concentrations. This is mainly due to the difference in the radii of metal ions: 68 pm for Ti^{4+} and 72 pm for Cu^{2+}. As mentioned above, the possible configurations of Cu-doped TiO_2 significantly increase with the increase in Cu concentration. In order to compare the relative stability of the different configurations with the same Cu concentration, some Cu-doped TiO_2 with isolated Cu arrangements are calculated for comparison. The defect formation energies are

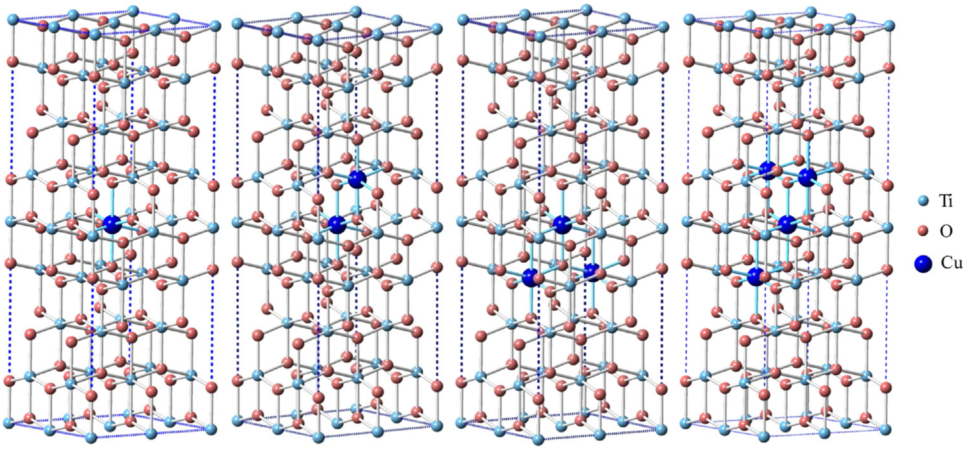

Fig. 1. $2 \times 2 \times 2$ Anatase TiO_2 supercell models of Cu-doped TiO_2 with clustered Cu arrangements. (a) 1 Cu atom, (b) 2 Cu atoms, (c) 3 Cu atoms, (d) 4 Cu atoms. Cu atoms are magnified for visual clarity.