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Dissertation

Electronic, Quasiparticle, and Thermodynamic Properties of Titanium Dioxide and Its Related Materials: A Systematic First-principles Study

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Abstract

In this dissertation, we report electronic and thermodynamic properties of titanium dioxide (TiO_2) and its related materials based on the density-functional theory (DFT), the GW method, and the density-functional perturbation theory (DFPT). Since the discovery of photocatalytic water-decomposition reaction using a titanium dioxide (TiO_2) electrode, a number of experimental and theoretical studies have been conducted and TiO_2 has been found to possess notable photocatalytic properties. A major drawback of TiO_2 as a photocatalytic material, however, is that TiO_2 is not photoactive under visible light. Therefore, a number of studies have been devoted to discover titanium-oxide-based visible-light-active photocatalytic materials and the DFT-based first-principles calculation has been playing a key role in designing and predicting properties of such new materials. Also, TiO_2 is a highly polymorphic material and as many as eleven crystalline phases have been identified so far. Therefore, exploring properties of various phases is of high importance. On the other hand, static DFT studies cannot approach several important properties such as the quasiparticle band stricture and thermodynamic properties. Therefore, applying first-principles methods beyond the static DFT, i.e. the Green's function many-body perturbation theory and the density-functional perturbation theory (DFPT), should be essential. We have mainly two purposes in this dissertation. First, we design, propose, and analyze new titanium-oxide-based visible-light-active photocatalytic materials based on conventional and state-of-the-art first-principles methods. Secondly, we test the predictive ability of several state-of-the-art first-principles methods on the properties that are not approachable within the static DFT method through the application to titanium dioxide systems. To achieve these purposes, we conducted the following three studies. First, we analyze the synthesis condition and electronic structures of heavily nitrogen-doped TiO_2 based on the DFT. Secondly, we study quasiparticle properties of pristine

rutile, pristine antase, and so-called "black" TiO_2 based on the GW method, one of the Green's function many-body perturbation theory. We also study the electronic properties of dilutely nitrogen-doped TiO_2 and titanium oxynitride within the DFT for comparison. Third, we study lattice-dynamical and thermodynamic properties of TiO_2 systems. In the first study, we propose a number of structural models for heavily nitrogen-doped TiO_2 and analyze the synthesis condition and the electronic structure of those systems. It is found that heavily nitrogen-doped TiO_2 shows sizable reduction of the band-gap value if we sufficiently dope nitrogen into TiO_2. We also show that such high-concentration doping is achievable and propose proper synthesis conditions based on the energetics. In the second study, we analyze quasiparticle band structures and other related properties based on the GW method. In contrast to the static DFT, the result shows that the GW method well reproduces the fundamental band-gap values of pristine TiO_2 systems and the corrections for the band-gap value by the GW method are larger than 1 eV. We also propose the structural models for black TiO_2. Although these structural models are rather simple and do not assume the existence of any vacancies nor impurities, it is found that the models possess smaller band-gap values than pristine rutile and anatase by more than 1 eV in accord with some experimental observations. In addition, we analyze the electronic properties of dilutely nitrogen-doped TiO_2 both for rutile-structured and anatase-structured systems within the DFT. It is found that low-concentration nitrogen doping is effective to reduce the minimum photoexcitation energy only for the anatase-structured systems. We also propose the structural models for titanium oxynitride and analyze the electronic properties within the DFT. We found that several proposed models of ours possess smaller band-gap values than those of anatase by more than 1 eV. In the third study, we obtain the temperature dependence of structural, elastic, and energetic properties of pristine TiO_2 systems by including the phonon effects based on the DFPT. The lattice-parameter values are in good agreement with the experimental data and the prediction errors are within only 1 percent in a wide range of temperature. Also, the prediction errors for bulk-modulus values are within 7 percent. The error for bulk modulus is significantly reduced from that of static DFT. We also address the phase transition of TiO_2 based on the free energy obtained from the DFPT and the quasiharmonic approximation. The results propose sophisticated ways to achieve titanium-oxide-based visible-light-active photocatalytic materials and show the importance of the implementation of first-principles methods beyond the static DFT.