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Interfacial charge transfer and mechanisms of enhanced photocatalysis of an anatase TiO_2(0 0 1)-MoS_2-graphene nanocomposite: A first-principles investigation

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ABSTRACT

First-principles calculations based on density functional theory were performed to investigate the interfacial properties of an anatase TiO_2(0 0 1)-MoS_2-graphene nanocomposite and gain insights into the role of interfaces on its overall photocatalytic performance. The geometric and electronic structures and charge-transfer characteristics of TiO_2(0 0 1)-MoS_2-graphene were explored in detail. A projected density of states analysis revealed that multipoint electron transfer from TiO_2 to MoS_2 and graphene greatly reduced the recombination of charge carries and prolonged electron lifetimes. Moreover, charge carriers were either more effectively separated as holes or electrons in the built-in electric fields on the TiO_2 or GR sides of the TiO_2(0 0 1)-MoS_2-graphene nanocomposite, respectively. Electron-hole recombination was thereby effectively suppressed, contributing to the material's enhanced photocatalytic performance. The calculated results were in agreement with reported experimental observations (Xiang et al., 2012) and provided new insights into the design of TiO_2-semiconductor-graphene tricomponent photocatalysts.

1. Introduction

The photocatalytic properties of semiconductor-based nanocomposites have been utilized in a variety of fields. Example applications of these photocatalysts include the production of hydrogen, the reduction of carbon dioxide and the degradation of organic pollutants via photocatalytic transformations [1–3]. Titanium dioxide (TiO_2) is generally considered to be a promising photocatalyst, because of its low cost, nontoxicity, and excellent physical and chemical stability. However, the wide band gap (3.0–3.2 eV) and the high charge-carrier recombination rate of photogenerated electrons (e^-) and holes (h^+) in TiO_2 significantly limit its use in practical applications [4,5]. In order to improve the photocatalytic performance of TiO_2, heterojunctions containing narrow band gap semiconductors have been used to absorb a broader range of wavelengths of light and to minimize the charge-carrier recombination rate. In recent decades, many bicomponent photocatalysts (including nano-TiO_2) have been reported, such as BiOI/TiO_2 [6], CdS/TiO_2 [7], alpha-Fe_2O_3/TiO_2 [8], SnS_2/TiO_2 [9], CuO/TiO_2 [10], g-C_3N_4/TiO_2 [11], and TiO_2/LMS (LMS = MoS_2, WS_2 or SnS_2) [12]. Although their photocatalytic performances are superior to that of pure TiO_2, these nanocomposites still suffer from the need to achieve a high charge-separation efficiency and a strong redox ability by isolating photogenerated e^- and h^+ [13,14].

To further improve the charge-separation efficiency of multicomponent TiO_2-based photocatalytic systems, Akitada et al. developed a tricomponent photocatalyst, TiO_2-Au-CdS [15], which displayed a higher photocatalytic activity than that of Au-TiO_2 and TiO_2-CdS. Au nanoparticles improved the charge-carrier separation between the TiO_2 and CdS [14,16]. However, the high cost and low abundance of Au limit its usefulness for practical applications. Graphene (GR) is a well-known two-dimensional nonmetallic conductive material that is able to capture and rapidly transfer the photogenerated electrons from a photocatalyst. For this reason, GR has become a strong candidate for replacing noble metals and improving the migration of photogenerated electrons. Yu and coworkers reported a pioneering TiO_2-MoS_2-GR nanocomposite [17], which achieved a high H_2 production rate of 165.3 μmol h^{-1} under ultraviolet (UV) irradiation. Subsequently, a series of tricomponent photocatalytic systems including GR and nano-TiO_2 have been reported, including TiO_2-CdS-RGO [18,19], TiO_2-Ag_3VO_4-GR [20], TiO_2-SnO_2-RGO [21], TiO_2-Ag_3PO_4-GO [22], TiO_2-MnO_x-GO [23], TiO_2-BiO_2CO_3-GR [24], and GR-Eu_2O_3-TiO_2 [25] where GO

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and RGO are graphene oxide and reduced graphene oxide, respectively. In these tricomponent photocatalysts, GR plays a significant role in improving the migration of photo-induced electrons and supporting the TiO_2 and other semiconductor nanoparticles. Simultaneously, the narrow band gap semiconductor acts as a photosensitizer, broadening the catalyst's absorption spectrum. These novel tricomponent photocatalysts have multiple integrated advantages, such as enhanced photocatalytic activities and improved visible light absorptions, which alter the direction of electron transfer and efficiently prohibit the recombination of charge carriers. For instance, the optimal H_2 production rate obtained on TiO_2-MoS_2-GR is more than 39 or 4 times those achieved by either TiO_2 or TiO_2-MoS_2 [17], respectively. These enhanced photocatalytic activities were believed be the results of the synergistic effects of GR and the other semiconductor in these nanocomposites [17,18], and a tentative mechanism was proposed for their prolonged electron lifetimes based on Z-scheme electron transfer [14,18]. Overall, these previous efforts have focused on designing and synthesizing novel tricomponent photocatalytic systems and experimentally evaluating their catalytic performances. Although some possible photocatalytic mechanisms have been proposed, the geometric structures and energetic properties at the interfaces of the different atomic layers remain unclear. More importantly, fundamental and insightful information is lacking regarding the effects of the interfacial composition and the electron transfer mechanisms of tricomponent photocatalysts at an electronic-structure level. To the best of our knowledge, a prior comprehensive theoretical study of tricomponent photocatalyst has not been reported to date.

Some theoretical investigations have been performed on bicomponent photocatalysts using density functional theory (DFT) [26–29]. For instance, Gao et al. found that an enhancement in photocatalytic performance was attributed to the hybridization of GR, resulting in a clear red shift in the absorption edge of TiO_2-GR [26]. Cao et al. reported that the efficient photosensitization of MoS_2 facilitated electron transfer between MoS_2 and the TiO_2(0 0 1) slab, resulting in an enhanced visible-light response [28]. In the work reported here, TiO_2-MoS_2-GR was chosen for the computational model as a representative tricomponent photocatalyst. It should be noted that catalytic performance primarily depends on the presence of key active sites, such as sharp corners, edges, and surfaces [30]. These active sites can be observed experimentally using transmission electron microscopy (TEM) [17,18,31]. Therefore, the computational models used in this work were abstracted from certain key component interfaces, which are contained in nanoscale microcrystals, as shown in Fig. 1. Because the interfacial properties of TiO_2-GR, TiO_2-MoS_2, and MoS_2-GR have been reported in previous studies [26–29], these interfaces are not considered, although they may be present in TiO_2-MoS_2-GR. Herein, a fundamental understanding of the geometric and electronic structures and charge transfer characteristics of TiO_2-MoS_2-GR is pursued using DFT calculations. The two built-in electric fields at the TiO_2(0 0 1)-GR and MoS_2-GR interfaces were found to enhance the separation of photogenerated carriers while effectively avoiding e^--h^+ pair recombination. These findings were in good agreement with previous experimental results [17]. These DFT calculation results aid in understanding the mechanisms of enhanced photocatalysis by a TiO_2-MoS_2-GR nanocomposite.

2. Computational details

2.1. Crystal surface

In general, there are three different crystallographic forms of TiO_2: rutile (tetragonal, $P4_2/mnm$), anatase (tetragonal, $I4_1/amd$), and brookite (orthorhombic, $Pbca$) [32]. Among these forms, anatase TiO_2 is the most common crystal phase observed under hydrothermal synthesis conditions [17,33]. Since TiO_2-MoS_2-GR and other TiO_2-GR-semiconductor composites are mainly synthesized hydrothermally, the photocatalytic properties of anatase TiO_2 are the focus of this work. Based on previous experimental and theoretical studies, the anatase TiO_2 (0 0 1) facet is dominant on a GR substrate for the photocatalytic production of H_2 and the degradation of organic dyes [26,34–37]. Therefore, the (0 0 1) facet of TiO_2 was cleaved into a section made up of two layers of Ti atoms, and a 6 × 3 TiO_2 supercell surface was built containing 108 atoms with optimized lattice parameters ($a \times b$) of 22.997 Å × 9.709 Å. In order to match the surface of the TiO_2 supercell, a $5\sqrt{3} \times 4$ GR supercell containing 80 atoms was constructed. The optimized lattice parameters of GR were 21.380 Å × 9.875 Å. According to previous theoretical studies, a monolayer of MoS_2 is suitable for model-based calculations used to explore the electronic properties of MoS_2-TiO_2 heterojunctions [27,28]. In this work, a $4\sqrt{3} \times 3$ MoS_2 monolayer supercell surface containing 72 atoms was built with optimized lattice parameters of 22.208 Å × 9.618 Å. As shown in Table 1, the mismatch between the optimized lattices of the three supercell surfaces was less than 4%. Through the combination of these three supercell surfaces a computational model was constructed containing TiO_2 in different locations within the same periodic microcrystal, as shown in Fig. 1. The different computational models are referred to as TiO_2(0 0 1)-MoS_2-GR, MoS_2-GR-TiO_2(0 0 1), and GR-TiO_2(0 0 1)-MoS_2. A 15 Å vacuum layer was added along the z axis of all of the computational models to prevent interactions between the periodic layers. All of the atoms were relaxed in the geometric optimization.

2.2. Theoretical calculations

Calculations were performed using the generalized gradient approximation (GGA), as implemented in the DMol^3 module [38,39] of the Materials Studio package. The electronic exchange and correlation energy were treated with the Perdew-Burke-Ernzerhof (PBE) [40] functional using the double-numeric quality basis set DND 3.5. DFT semi-core pseudopots (DSPPs) were used to treat the core electrons. The convergence criteria for the geometric optimization of the energy and maximum force tolerances were 2.0×10^{-5} Ha and 0.004 Ha Å^{-1}, respectively. The Monkhorst-Pack k-points value at the Brillouin zone depended on the size and shape of the unit cell. Consequently, energy convergence was tested with a variable number of k-points for the GR, TiO_2(0 0 1), and MoS_2 supercells, and detailed results are provided in Table S1 in the supporting information (SI). A favorable k-point value of 4 × 8 × 1 was selected for geometric optimizations and energy calculations in each of the models.

Because of the absence of strong bonding interactions between the atomic layers, van der Waals (vdW) forces contribute significantly to the total energy. However, since the standard PBE functional fails to describe weak interactions, an empirical dispersion-corrected DFT-D approach based on Grimme [41,42] was used to better describe the atomic layers' non-bonding interactions.

The total energy ($E_{PBE\text{-}D}$) is given by

$$E_{PBE\text{-}D} = E_{PBE} + E_{disp} \tag{1}$$

where E_{PBE} is the electronic energy as obtained from PBE and E_{disp} is the empirical dispersion correction term given by [42]

$$E_{disp} = -s_6 \sum_{i=1}^{N_{at}-1} \sum_{j=i+1}^{N_{at}} \frac{C_6^{ij}}{R_{ij}^6} f_{dmp}(R_{ij}). \tag{2}$$