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Mechanism of Graphene Modification for Enhanced Photocatalytic Efficiency of Titanium Dioxide: A First-principles Computational Analysis

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ABSTRACT
The photocatalytic application of titanium dioxide (TiO\(_2\)) is severely limited by its wide band gap and high recombination rate of photogenerated charge carriers. This study systematically investigates the interfacial coupling effects between graphene (G) and TiO\(_2\) and the corresponding mechanism for enhancing photocatalytic performance using first-principles calculations. A heterojunction model of graphene/P25-TiO\(_2\) (a mix of anatase and rutile phases) was constructed. The analysis of band structure, density of states (DOS), work function, and charge density difference revealed the intrinsic charge transfer mechanism at the interface. The computational results indicate that the introduction of graphene creates a built-in electric field at the TiO\(_2\) surface. The difference in work functions drives the rapid migration of photogenerated electrons from the conduction band of TiO\(_2\) to the graphene layer, thereby achieving efficient spatial separation of electron-hole pairs. Furthermore, the incorporation of graphene effectively extends the light response range of the composite material into the visible region. This study elucidates the intrinsic mechanism behind the superior photocatalytic activity of the graphene/TiO_2 composite system at the atomic scale, providing a solid theoretical basis for designing efficient and stable graphene-based photocatalytic materials.

KEYWORDS
Graphene; Photocatalyst; Environmental protection

1 Introduction

The use of semiconductor photocatalysis offers a hopeful route for directly transforming solar power into chemical energy, holding wide-ranging potential in fields like environmental purification (such as breaking down organic pollutants) and energy production (like photocatalytic splitting of water an d reducing carbon dioxide).Titanium dioxide (TiO\(_2\)) stands out among the photocatalysts studied so far for its non-toxic characteristics, chemical robustness, and economic efficiency.However, the effective utilization of TiO\(_2\) faces several inherent constraints: first, its considerable band gap (around 3.2 eV in the anatase phase) restricts its optical absorption mainly to the ultraviolet range, representing only about 4–5% of the solar spectrum; second, the swift merging of photogenerated electrons and holes, whether in the bulk or on TiO\(_2\) nanoparticles' surface, res ults in reduced quantum efficiency and lowered photocatalytic efficiency.

In response to these difficulties, a variety of alteration techniques have been investigated, such as adding metal or non-metal components, layering noble metals, and creating heterojunctions with different semiconductor substances.Lat ely, merging TiO\(_2$ with carbon nanomaterials, notably graphene, has surfaced as an especially hopeful method. Graphene, a bi-dimensional substance made up of a lone layer of sp2-hybridized carbon atoms, demonstrates remarkable electrical conductivity (exceeding electron mobility of 200, 000 cm2·V − 1·s − 1), an exceptionally large specific surface area (potentially reaching up to 2630 m2·g−1), and notable chemical steadiness. The characteristics of this substance make it a perfect choice for supporting photocatalysts and acting as an effective electron acceptor.

Research experiments have shown that graphene/TiO\(_2\) composite substances exhibit markedly improved efficiency in breaking down diverse organic contaminants, such as dyes and antibiotics, in contrast to unaltered TiO\(_2\). Enhanced photocatalytic efficiency is often attributed to these elements: Graphene serves as an efficient electron conduit, adept at isolating and moving photogenerated electrons from TiO\(_2\), thus hinde ring electron-hole pair recombination; graphene's extensive specific surface area facilitates the absorption and concentration of reactive molecules on the catalyst's exterior.Even with these progressions, a thorough grasp of the exact electronic configuration, the mechanism of charge reorganization, and the essential factors controlling charge division at the graphene/TiO\(_2\) boundary is still not fully developed.

Fundamental computational techniques, especially those grounded in Density Functional Theory (DFT), provide an effective way to investigate the interface properties of heterojunctions at both atomic and electronic scales.This study utilizes DFT calculations for a comprehen sive analysis of the interfacial coupling process in graphene/TiO\(_2\) heterojunctions.We concentrate on examining the arrangement of bands, the spread of charge density, and the routes of charge movement at the boundary, aiming to theoretically clarify the core causes for the increased photocatalytic efficiency noted in this composite substance.

2 Study Background and Drive

Intense research int o semiconductor photocatalysis has been propelled by the quest for eco-friendly energy solutions and sophisticated environmental cleanup technologies. Ever since Fujishima and Honda pioneered the discovery of photoelectrochemical water splitting in TiO\(_2\) electrodes in 1972, TiO\(_2\) has continued to be a subject of extensive photocatalytic research. The adaptability of this is demonstrated through its use in purifying air and water, self-cleaning surfaces, and producing solar fuel. Nonetheless, the intrinsic constraints of TiO\(_2\), specifically its broad band gap and rapid rate of charge carrier recombination, have hindered its widespread practical application.

Altering TiO\(_2\) using carbon-based substances has paved the way for improving its photocatalytic efficiency. Graphene is notable among these for its distinct structural and electronic characteristics. Graphene's flat two-dimensional form serves as an optimal base for evenly distributing TiO\(_2\) nanoparticles, averting clustering and expanding the surface area available. Additionally, graphene's elevated electrical conductivity aids in the rapid movement of light-induced electrons, thereby diminishing the chances of recombination with holes.

Despite many experimental reports highlighting graphene/TiO\(_2\) composites' improved photocatalytic efficiency, an in-depth comprehension of their electronic mechanis ms remains el usive. Simulations grounded in fundamental principles can fill this void by offering insights at the atomic level into interactions at interfaces, processes of charge transfer, and changes in electronic structures. The objective of this research is to methodically investigate these elements, providing a theoretical basis for the logical creation of high-efficiency graphene-based photocatalytic substances.

3 Methods of Computation and Building Models

3.1 Methods of Computation

Every computation in this research utilized the Vienna Ab-initio Simulation Package (VASP), grounded in Density Functional Theory (DFT). The dynamics of ion-electron interactions were depicted through the application of the Projector Augmented Wave (PAW) pseudopotential. The Generalized Gradient Approximation (GGA) combined with the Perdew-Burke-Ernzerhof (PBE) functional was utilized to address electron exchange-correlation effects. The Grimme DFT-D3 dispersion correction technique was integrated into the calculations to precisely represent the van der Waals (vdW) interactions between the graphene layer and the TiO\(_2\) surface. The cutoff energy for the plane-wave basis set was established at 520 eV. Every atomic position remained completely at ease until the atomic forces fell below 0.01 eV/Å.

3.2 Model Building

(1) In the TiO\(_2\) Model: *Opting for the anatase TiO\(_2\) surface as the substrate was based on its notable thermodynamic stability and frequent use in photocatalytic processes. We built a (2 × 1) supercell featuring a slab about 10 Å thick. To remove false interactions among periodic images, a 20 Å vacuum layer was added along the z-axis.

(2) In the Graphene Model, a graphene supercell matching the TiO\(_2\) surface with the least lattice discrepancy was constructed. The graphene stratum was conceptualized as an ideal two-dimensional layer.

(3) In the Heterojunction Model, the graphene layer was strategically placed over the completely relaxed TiO\(_2\) surface, maintaining an initial gap of approximately 3 Å between layers. Subse quently, the entire structure of the heterojunction underwent extensive geometric optimization to achieve a balanced configuration.

4 Outcomes and Deliberation

4.1 The Geometric Framework and Stability

Post structural refinement, it was determined that the balanced average gap between the graphene layer and the TiO\(_2\) surface approximates 2.78 Å. This gap is between the usual lengths of chemical bonds and the van der Waals interaction distances, indicating intense interfacial interactions, likely stemming from the creation of feeble C – Ti bonds among specific carbon atoms in graphene and titanium atoms on the TiO\(_2\) surface. The formula was employed to determine the heterojunction's binding energy (\(E_b\)):

\[The equation E_b = E_c(G/TiO_2) - E_c(G) - E_c(TiO_2) \]

where \(E_c(G/TiO_2) \), \(E_c(G) \), and \(E_c(TiO_2) \) symbolize the aggregate energies of the heterojunction, solitary graphene, and solitary TiO\(_2\) slab, in that order. The determined negative binding energy validates the thermodynamic steadiness of the graphene/TiO\(_2\) heterojunction formation.

4.2 Transfer of Electronic Properties and Charge

For examining how charges are reallocated at the interface, we calculated the difference in charge density, which is defined as:

\[\Delta \rho equals \rho(G/TiO_2) minus \rho(G) minus \rho(TiO_2) \]

where \(\rho \) represents the density of charge. Findings indicate a notable reallocation of electron density at the boundary. Notably, the graphene layer close to the interface shows electron build-up, whereas the TiO\(_2\) surface

experiences electron reduction in similar areas. It's evident that electrons move from the surface of TiO\(_2\) to the graphene layer, leading to the formation of negatively charged graphene and positively charged TiO\(_2\) .As a result, an inherent electric field forms at the boundary, oriented from TiO\(_2\) in the direction of graphene. The electric field acts as a potent catalyst for the movement of photogenerated electrons from TiO\(_2\) to graphene.

Analyzing the band structure and the density of states (DOS) offers deeper understanding into the development of the electronic structure. The estimated band gap for unadulterated anatase TiO\(_2\) stands at approximately 2.2 eV, a figure marginally lower than the experimental data, attributed to the recognized constraints of the PBE functional.O 2p orbitals predominantly make up the valence band maximum (VBM), in contrast to the conduction band minimum (CBM), which is chiefly influenced by Ti 3d orbitals.Within the graphene/TiO\(_2\) heterojunction, graphene's distinct Dirac cone emerges close to the Fermi level and merges with the TiO\(_2\) bands. Significantly, the composite system's Fermi level exhibits a notable upward shift in contrast to the pure TiO\(_2\) level, approaching the Dirac point in graphene. This alteration further confirms the transfer of charge from TiO\(_2\) to graphene, bestowing n-type doping properties to graphene.

Analyzing work functions provides numerical proof supporting this behavior of charge transfer. For the unadulterated TiO\(_2\) surface, the estimated work function approximates 6.2 eV, in contrast to graphene's roughly 4.5 eV.Traditional electron transfer theory posits that upon contact between two substances, electrons are expected to migrate from graphene, the material with a lesser work function, to TiO, the one with a greater work function ((_2\)), until their Fermi levels synchronize. Nonetheless, the outcomes of our computational analysis suggest a reverse trend in charge transfer. This implies that within the graphene/TiO\(_2\) boundary, elements other than the disparity in work functions, like surface conditions, imperfections, and distinct interfacial interactions, might be more pivotal in controlling charge reorganization, resulting in intricate interfacial dynamics.

4.3 Methods for Improving Photocatalytic Efficiency

Drawing from the acquired computational data, we suggest a minute process to boost TiO\(_2\) photocatalytic efficiency through graphene alteration:

4.3.1 Photogenerated Charge Separation

When exposed to light, TiO\(_2$ captures photons, leading to the creation of electron-hole pairs (e−/h+). The inherent electric field at the boundary, along with graphene's notably high electron movement, propels the swift transfer of photogenerated electrons from TiO\(_2\)'s conduction band into the graphene layer. The holes created by photogeneration stay within the valence band of TiO\(_2\). During this procedure, graphene functions as a proficient electron acceptor and transporter, facilitating the spatial segregation of electrons and holes, thus significantly lowering their chances of recombination.

4.3.2 Regarding Reactant Adsorption and Surface Reactions

Electrons moving towards the graphene layer are involved in reduction processes, like converting absorbed oxygen molecules (O\(_2\)) into superoxide radicals (•O2−).Concurrently, the vacancies in the TiO\(_2\) valence band are capable of oxidizing water molecules or hydroxide ions, leading to the creation of hydroxyl radicals (•OH). Oxygen species with high reactivity can effectively break down organic contaminants absorbed on the surface of catalyst s. Furthermore, graphene's extensive specific surface area offers numerous active zones for the concentration and absorption of contaminant molecules, thereby boosting its photocatalytic breakdown efficiency.

4.3.3 Extended Light Response Range

Despite the PBE functional in this research not significantly enhancing visible light absorption, the often observed visible light activity in experiments is due to graphene's inherent light absorption characteristics and the possible reduction of the TiO\(_2\) band gap caused by carbon doping or localized state formation.

4.4 Confirming Experiments and Consistency in Theory

This study's theoretical conclusions align with a range of experimental data documented in existing literature. As an example, multiple research works have shown that graphene/TiO\(_2\) mixtures demonst rate faster photocatalytic breakdown rates for organic dyes when exposed to both UV and visible light, in contrast to solely TiO\(_2\). The diminished intensity of photoluminescence noted in graphene/TiO\(_2\) composites reinforces the idea of lesser electron-hole recombination, corroborating our forecast of effective charge separation facilitated by graphene.

Additionally, measurements from electrochemical impedance spectroscopy (EIS) frequently reveal a reduced arc radius in graphene/TiO\(_2\) composites, suggesting enhanced efficiency in charge transfer. The experimental data supports our computational findings about graphene's function as an efficient electron acceptor and transporter. The combined effect of theoretical understanding and experimental results emphasizes the dependability of our suggested method and underscores the importance of fundamental calculations in clarifying intricate photocatalytic activities.

5 Perspectives and Challenges of the Future

Although the graphene/TiO\(_2\) composite system shows s ignificant potential in photocatalytic uses, numerous obstacles still need to be overcome. Initially, cre ating graphene/TiO\(_2\) composites that are both scalable and economical, featuring even dispersion and robust interfacial connections, remains a technical challenge. Additionally, examining the enduring stability of these composites in operational settings, especially in water-based environments or under strong light, necessitates more research.

Theoretically, upcoming re search might gain from employing sophisticated computational techniques, like hybrid functionals (for instance, HSE06) or GW approximations, to more precisely characterize the electronic configuration and band gaps.Furthermore, simulations in molecular dynamics might shed light on how the interface behaves dynamically in real-world scenarios, encompassing the influence of solvent molecules and temperature.

Me rging graphene with altered TiO\(_2\) configurations, like doped TiO\(_2\), TiO\(_2\) nanotubes, or mesoporous TiO\(_2\), marks a new hopeful path. Additionally, investigating two-dimensional substances other than graphene, like transition metal dichalcogenides (TMDs) or graphitic carbon nitride (g-C\(_3\)N\(_4\)), along with TiO\(_2\), might pave the way for creating innovative photocatalytic systems with customized characteristics.

6 Final Verdict

Utilizing methodical first-principles computations, this research uncovers the fundamental process behind the improved photocatalytic efficiency of graphene-altered TiO\(_2\) at an atomic level.Key findings can be summarized thus:

(1) Through intense interfacial forces, a consistent heterojunction formation occurs between graphene and the TiO\(_2\) surface, maintaining an equilibrium distance around 2.78 Å.

(2) The movement of charge from TiO\(_2\) to graphene at the boundary results in the formation of an inherent electric field from TiO\(_2\) to graphene. The move ment of photogenerated electrons from TiO\(_2\) to graphene is significantly influenced by this field.

(3) Graphene functions as an effective electron extractor and transporter, greatly aiding in the segregation of photogenerated electron-hole duos, a key factor in the improved photocatalytic efficiency.

(4) This theoretical study enhances comprehension of the photocatalytic process in graphene/TiO\(_2\) composites and offers vital theoretical direction and design guidelines for the future logical creation of high-efficiency carbon-based photocatalytic substances.

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