

The electronic structure and photoactivity of TiO₂ modified by hybridization with monolayer g-C₃N₄

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ABSTRACT

In this work, first-principles calculation based on density functional theory (DFT) was used to study the enhanced photocatalytic mechanism of TiO₂ hybridized with pristine and defective g-C₃N₄ systematically. The theoretical investigations on both geometry structure and electronic properties, involving band structure, density of states, electron population and charge density difference, were carried out to characterize the improved property of TiO₂. It was found that the combination TiO₂ with g-C₃N₄ could be verified for high thermodynamic stability. The interaction between TiO₂ and g-C₃N₄ led to form a built-in electric field at the interface, which facilitated the separation of electron-hole pairs and restrained photo-generated carrier recombination. Furthermore, electrons transiting from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) promoted the separation of electrons and holes. The effective separation of electron-hole pairs prolonged the lifetime of carries and enhanced the photocatalytic activity of TiO₂/g-C₃N₄. The theoretical investigations could verify the experimental observation results [Chem. Sci., 5(2014), 3946–3951, Phys. Chem. Chem. Phys., 17(2015), 17406–17412] and illustrate the mechanisms of photocatalytic enhancement of TiO₂/g-C₃N₄ composite photocatalysts. Furthermore, the calculated optical absorption curves demonstrated that the absorption edge of TiO₂/g-C₃N₄ composites shifted to visible-light region and its photocatalytic activity increased under visible-light irradiation. The theoretical investigation might provide referable and valuable information for understanding the observed enhanced photocatalytic mechanism in experiments.

1. Introduction

The environmental pollution and energy crisis are attracting increasingly attention, with social development and industrialization in the past decades [1]. Since Fujishi and Honda discovered the phenomenon of photocatalytic water splitting of TiO₂ under ultraviolet irradiation [2–4], TiO₂ has received intensive attention as a promising photocatalysts, especially in environmental pollution control [5]. However, due to its wide energy gap (3.0–3.2 eV) and easy recombination of photo-generated electron-hole (e⁻-h⁺) pairs, which resulted in low efficiency of photocatalysis, the applicability of TiO₂ has been limited practically [6]. Therefore, it is really meaningful to take urgent measures to reduce the recombination of e⁻-h⁺ pairs and enhance the photocatalytic activity of TiO₂. Many strategies have been taken to enhance the photocatalytic performance of TiO₂, including doping with metallic or non-metallic elements and forming a heterojunction with other semiconductors [7]. Among these various methods,

combining with other semiconductors to form a heterojunction seemed to be an effective way to improve photocatalytic activity and extend the visible-light-response region of TiO₂ [8]. The built-in electric field of heterojunction could drive the photo-generated e⁻-h⁺ to transfer to contrary directions, consequently depressing their recombination [9]. It was the key to choose an appropriate semiconductor to combine with TiO₂ to construct a TiO₂-based heterostructure with high photocatalytic activity.

Graphitic carbon nitride (g-C₃N₄), as a stable, nontoxic and novel polymeric organic semiconductor, has attracted attentions in the photocatalysis field [10,11]. The energy gap of g-C₃N₄ is 2.7 eV, which makes it a more attractive photocatalytic activity in the visible light region and exhibit excellent sunlight utilization [12,13]. However, it has the drawback of high recombination of photo-generated carriers [14]. But fortunately, due to the well-matched energy levels between g-C₃N₄ and TiO₂, the photo-generated e⁻-h⁺ could be easily separated in g-C₃N₄/TiO₂ composite [15]. For example, g-C₃N₄-TiO₂ Z-scheme

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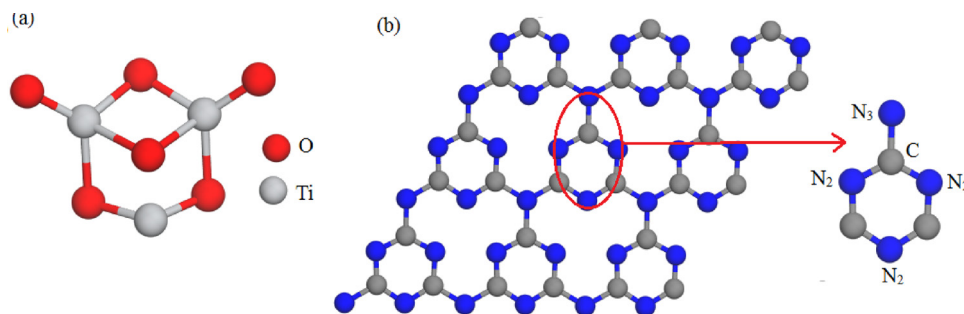


Fig. 1. The Crystal structure, (a) $(\text{TiO}_2)_3$ cluster, (b) $\text{g-C}_3\text{N}_4$ monolayer. The light gray and red balls represent Ti and O atom, while the deep gray and blue balls represent C and N atom, respectively (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

composite synthesized via introducing $\text{g-C}_3\text{N}_4$ nanoparticles cover the surface of TiO_2 , showed significant photocatalytic performance for formaldehyde decomposition in air [16]. H. Li et. al. have demonstrated a facial solvothermal method to synthesize $\text{TiO}_2/\text{g-C}_3\text{N}_4$ composite for improved photocatalytic degradation of phenol [17]. The photocatalytic activity of core-shell $\text{TiO}_2@/\text{g-C}_3\text{N}_4$ composite was almost 3 times higher than the activity of pure TiO_2 for degradation of rhodamine B under visible light [18]. It was reported that C-doped $\text{TiO}_2@/\text{g-C}_3\text{N}_4$ core-shell hollow nanospheres were prepared, which exhibited remarkably enhanced visible-light photocatalytic activity for water splitting [19]. Cooperated with photosensitizer gold, $\text{g-C}_3\text{N}_4$ not only promoted the efficient transfer and separation of photogenerated electron-hole pairs, but also retained the strong redox ability of the charge carriers, which remarkably enhanced the photocatalytic performance of C- TiO_2 photocatalyst for H_2 evolution rate under visible-light irradiation [20].

In view of above studies, $\text{g-C}_3\text{N}_4$ could serve as a suitable candidate to be composited with TiO_2 and enhance its photocatalytic performance. However, there might appear intrinsic points defects in the material synthesis process, which affected the electronic structure and also probably acted as specific reaction sites [21]. These defects could provide trapping sites for photoinduced carriers and hinder $e^- \cdot h^+$ recombination to improve the overall quantum efficiency [22]. For instance, nitrogen defects in $\text{g-C}_3\text{N}_4$ have enhanced photocatalytic H_2 evolution through broadening visible-light absorption and depressing $e^- \cdot h^+$ combination, and the average H_2 evolution rate was 3 times higher than that of pristine $\text{g-C}_3\text{N}_4$ [23]. The defective $\text{g-C}_3\text{N}_4$ enhanced visible light photocatalytic hydrogen production, which showed 4.8 times hydrogen increase as compared with pristine $\text{g-C}_3\text{N}_4$ [24,25]. Although some researchers have already illustrated excellent photocatalytic performance of d- $\text{g-C}_3\text{N}_4@/\text{TiO}_2$ in experiments, the mechanism of enhanced performance of defective $\text{g-C}_3\text{N}_4$ (d- $\text{g-C}_3\text{N}_4$) composited with TiO_2 remains unclear, nevertheless [26]. There is still a lack of corresponding theoretical research to further reveal the effect of interfacial composition and clarify the improved photocatalytic mechanism of d- $\text{g-C}_3\text{N}_4/\text{TiO}_2$ composite.

To clarify the enhanced photocatalytic mechanism of TiO_2 , the first-principle calculations based on density functional theory (DFT) was performed to characterize the interface properties between d- $\text{g-C}_3\text{N}_4$ and TiO_2 . The geometry structure and electronic properties, such as energy structure, density of states, charge population and density difference, as well as orbital distribution of TiO_2 cluster anchoring at $\text{g-C}_3\text{N}_4$ were investigated to illustrate the enhanced photocatalytic activities of $\text{g-C}_3\text{N}_4/\text{TiO}_2$ composites. It was found that there formed a polarized electric field at the interface region, which enhanced the separation of photo-generated carriers and inhibited $e^- \cdot h^+$ pairs recombination effectively. The theoretical study might provide reasonable and indispensable elucidation for the experimental investigation.

2. Computational details

All of the calculations are performed using the well tested Cambridge Serial Total Energy Package (CASTEP) code [27,28], which employs plane-wave basis sets to treat valence electrons and norm-conserving pseudopotentials to approximate the potential field of ionic cores. We employed generalized gradient approximation (GGA), the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional, and the ultrasoft pseudopotential in the calculations. During the structural optimization, the cutoff energy was set to be 400 eV, and structure relaxation was performed until the convergence criteria of energy and force reached 1×10^{-5} eV and $0.02 \text{ eV } \text{\AA}^{-1}$, respectively. Further increasing the cutoff energy brought minor difference in the calculation results. Monkhorst-Pack mesh of $2 \times 2 \times 1$ and $6 \times 6 \times 1$ k-points were used to sample the two-dimensional Brillouin zone for geometry optimization and electronic structure calculation, respectively.

S. A. Shevlin and S. M. Woodley have made a detailed investigation on $(\text{TiO}_2)_n$ cluster by DFT calculation [29]. It indicated that $(\text{TiO}_2)_3$ nanocluster was a suitable structural model to explore its structure and electronic properties, which has been proved to be in good agreement with the experimental data. To reduce the calculation time, we used the small stoichiometric $(\text{TiO}_2)_3$ cluster in our study based on the above consideration, which was presented in Fig. 1a. There are three triazine structure in monolayer $\text{g-C}_3\text{N}_4$ allotrope. And according to the different chemical environments, N atoms are divided into two types (N_2 and N_3). The N_2 atom only connects two C atom, leaving a non-bonding character. While N_3 atoms are fully saturated by the surrounding three C atoms and all C atoms are connected to the nearest N atoms, as shown in Fig. 1b. The distance between C and N_2 atom is 1.32 \AA , while the distance between C and N_3 atom is 1.45 \AA . To reflect the difference structure of the $\text{g-C}_3\text{N}_4$, we selected six representative structures including pristine $\text{g-C}_3\text{N}_4$ (p- $\text{g-C}_3\text{N}_4$), $\text{g-C}_3\text{N}_4$ with one C vacancy (d(C)- $\text{g-C}_3\text{N}_4$), $\text{g-C}_3\text{N}_4$ with one N_2 vacancy (d(N_2)- $\text{g-C}_3\text{N}_4$), $\text{g-C}_3\text{N}_4$ with one N_3 vacancy (d(N_3)- $\text{g-C}_3\text{N}_4$), $\text{g-C}_3\text{N}_4$ with two N_2 vacancies (d(N_2, N_2)- $\text{g-C}_3\text{N}_4$) and $\text{g-C}_3\text{N}_4$ with N_2 and N_3 vacancies (d(N_2, N_3)- $\text{g-C}_3\text{N}_4$), which were obtained by removing C atom or N atom from the structure. The models were showed in Fig. 2a-f. At last, we combined $(\text{TiO}_2)_3$ cluster with p- $\text{g-C}_3\text{N}_4$, d(C)- $\text{g-C}_3\text{N}_4$, d(N_2)- $\text{g-C}_3\text{N}_4$, d(N_3)- $\text{g-C}_3\text{N}_4$, d(N_2, N_2)- $\text{g-C}_3\text{N}_4$ and d(N_2, N_3)- $\text{g-C}_3\text{N}_4$ to form p- $\text{g-C}_3\text{N}_4/\text{TiO}_2$, d(C)- $\text{g-C}_3\text{N}_4/\text{TiO}_2$, d(N_2)- $\text{g-C}_3\text{N}_4/\text{TiO}_2$, d(N_3)- $\text{g-C}_3\text{N}_4/\text{TiO}_2$, d(N_2, N_2)- $\text{g-C}_3\text{N}_4/\text{TiO}_2$ and d(N_2, N_3)- $\text{g-C}_3\text{N}_4/\text{TiO}_2$ composites, respectively.

3. Result and discussion

3.1. Geometric structures and binding energies

Before exploring the properties of $\text{g-C}_3\text{N}_4/\text{TiO}_2$ composites, we first investigated the lattice structure of monolayer $\text{g-C}_3\text{N}_4$. The optimized lattice parameters $a = b = 4.778 \text{ \AA}$ were in well agreement with the previous experimental data ($a = b = 4.742 \text{ \AA}$) for monolayer $\text{g-C}_3\text{N}_4$ [30], which indicated the theoretical calculation was credible.

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