Synergistic effect of MoS$_2$/TiO$_2$ heterostructures with enhanced photo- and electro-catalytic performance

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Herein, different MoS$_2$/TiO$_2$ heterostructures are prepared with appropriate interface modifications. Electronic structure analysis shows that type II band alignments are realized at the interface, which efficiently drives the photo-excited charge to separate. Moreover, the band offsets can be delicately controlled by surface states with significant effect on their photocatalytic performance. In addition, the synergistic effect between MoS$_2$ and TiO$_2$ enhances the hydrogen evolution reaction (HER) activity of their hybrids which is tunable via interface engineering. The observed Tafel slope of 66.9 mV/dec for MoS$_2$/TiO$_2$-H complexes suggests the Volmer-Heyrovsky mechanism. The enhanced activities was attributed to the abundant active sites at the interfaces as well as the improved charge transfer efficiency.

TiO$_2$ is one of the most intensively studied photochemical materials with wide applications in environmental protection and green energy [1,2]. However, because of its large intrinsic band-gap, it is only sensitive to ultraviolet (UV) light and inefficient for solar light harvesting. To go beyond this, strategies such as foreign elements doing and formation of TiO$_2$ based heterostructures have been employed to broaden their light harvesting window into visible light range [3,4]. More recently, it was realized that electronic behaviors in surface layers play significant roles to photocatalytic performance and thus surface functionalization is substantial in the quest of visible light photocatalysis [4-7]. This offers new ideas for designing visible light photocatalysis via engineering the surface layer only.

On the other hand, owing to its great potentials in areas of photo-detection [8], photocatalysis [9], nanoelectronics [10], and optoelectronics [11], two dimensional (2D) molybdenum disulfide (MoS$_2$) has become widely studied functional material. With the appropriate band gap energy and high light absorption, MoS$_2$ could be suitable for applications in effective photovoltaic and photocatalysts under visible light. Coupling two materials to form one with novel functionalities has become a common method in material science studies. The function of MoS$_2$ in MoS$_2$/TiO$_2$ complexes is an effective sensitizer for enhanced production of hydrogen [12-14]. However, MoS$_2$ tends to form irregular aggregates of nanoparticles or stacked multilayers without strong chemical bonding with the substrates especially for its (001) planes where intrinsic van der Waals forces govern the interlayer interactions, which, in most of the time, disfavors charge transfer at the interface. For a given heterostructure system, interface band alignment is substantial to the electron-hole separation which is desired to be tunable in manners to enhance charge separation efficiency.

In previous study [15], it has been shown that type II band alignment is formed between MoS$_2$ thin film and single crystal rutile TiO$_2$. Recently, there are a few reports on synthesized MoS$_2$/TiO$_2$ heterostructures [16-23] with improved photocatalytic performance, which show that surface modifications of TiO$_2$ are generally needed to create more nucleation centers in order to form solid interfacial bonding [17]. However, the insight of this growth mechanisms and how the interface properties affect their growth behaviors and modulate the electronic structure are yet to be understood. Moreover, since MoS$_2$ layer is atomically thin, interfacial interaction are markedly pronounced in certain scenarios with strong effect on their charge transport properties [15].

Up to now, the most efficient hydrogen evolution reaction (HER) catalysts contain scarce Pt-group metals, which catalyze HER with almost zero overpotential. Recently, MoS$_2$ was found to be good HER catalyst and believed to hold strong promise for replacing Pt-based catalysts [24-27]. However, the low active sites and poor conductivity of pristine MoS$_2$ limit its electrocatalytic abilities [25]. Both experimental and theoretical work confirms that the HER activity of MoS$_2$ is strongly correlated with unsaturated S atoms along Mo-edges and defects in MoS$_2$ nanosheets [28-31]. However, the nano-sized MoS$_2$ with unsaturated edges sites are thermodynamically unstable and easy to curl up. The formation of MoS$_2$-based hybrid structures is one of the easy way to cover this issue. The key challenge for MoS$_2$-based complexes in the HER lies in accelerating electron transfer while maintaining rich active sites. This requires the control and design of interfacial properties to regulate interfacial band alignment for fast charge transfer. For a given heterostructure system, interface band alignment is substantial to the electron-hole separation. Therefore, the effect of interfacial band alignment on their HER-per-
In this work, MoS$_2$/TiO$_2$ hybrid complexes with various purposely modified interfaces have been successfully prepared. Type-II band alignment are formed in all cases making conduction band minimum (CBM) and the valence band maximum (VBM) occurred in different semiconductors. The VBM of MoS$_2$ was pushed up against that of TiO$_2$ on sulfuric acid (H$_2$SO$_4$) treated nanobelts. In addition, we found that sulfuric acid (H$_2$SO$_4$) treated samples exhibit much more enhanced HER activity which emphasizes the important roles that the interfacial build-in electric field plays for efficient electron transfer.

EXPERIMENTAL DETAILS

Rough surface of TiO$_2$ nanobelts and the corresponding MoS$_2$/TiO$_2$ heterostructures were fabricated by hydrothermal methods. Briefly, 0.1 g TiO$_2$ powder (P25) was mixed with 15 ml of 10 M sodium hydroxide (NaOH) solution and 15 ml deionized (DI) water. After stirring, the solution was transferred into a 50 mL Teflon-lined stainless steel autoclave followed by hydrothermal treatment at 210°C for 24 h. The white fluffy product was washed with DI water and 0.1 M HCl solution to get H-titanate nanobelts which was decomposed into TiO$_2$ nanobelts by annealing in O$_2$ (50 sccm) at 700 °C for 1 h. To increase the surface nucleation sites, the TiO$_2$ surfaces were treated with a combination of base and acid etching in three different manners: 1) Etching in 40 ml NaOH at 150 °C for 4h, followed by 0.1 M HCl for 3 h, labeled as TiO$_2$-NH thereafter; 2) Etching in 40 ml 0.02 M H$_2$SO$_4$ solution at 100 °C for 12 h, labeled as TiO$_2$-H thereafter; 3) Combination of steps 1) and 2) in sequence, labeled as TiO$_2$-NH-H thereafter. To get MoS$_2$/TiO$_2$ heterostructures, the mixture of 30 mg sodium molybate (Na$_2$MoO$_4$·2H$_2$O) and 60 mg thioacetamide (C$_2$H$_5$NS) was stirred in 30 ml DI water to form uniform and transparent solution. Then 20 mg different surface-modified TiO$_2$ powders were added and the mixture was transferred into Teflon-lined stainless steel autoclave. The autoclave was sealed and maintained at 220 °C for 24 h. The black product, MoS$_2$/TiO$_2$ complex, was obtained after separation and drying.

The structure phase of MoS$_2$/TiO$_2$ hybrids were characterized using x-ray diffraction (XRD, D8 FOCUS). The morphology of the powders were examined using scanning electron microscopy (SEM, Nova Nano SEM450) and transmission electron microscopy (TEM, JEM-2100F, JEOL 200 kV). The x-ray photoelectron spectroscopy (XPS) measurements were performed using VG ESCALAB 220i-XL instrument equipped with a monochromatic Al K$_x$ (1486.7 eV) x-ray source. All spectra were recorded in the constant pass energy mode with pass energy of 20 eV and step width of 0.1 eV. The electrochemical performance were tested in a three-electrode system (LK2010A) in 0.5 M H$_2$SO$_4$ using a Ag/AgCl (saturated KCl) reference electrode, a Pt counter electrode and glassy carbon (GC, 3 mm in diameter) electrode loaded with various catalysts as the working electrode. All the polarization curves were plotted after IR-correction.

RESULTS AND DISCUSSION

In order to examine the crystal phase of the TiO$_2$ nanobelts and MoS$_2$/TiO$_2$, XRD measurements are employed on as-prepared TiO$_2$, post-treated TiO$_2$ nanobelts, MoS$_2$/TiO$_2$ heterostructures and pure MoS$_2$ flowers. As presented in Figure 1(a)-(b), the detected diffraction patterns at 25.44°, 37.84° and 48.12° match well with the (101), (004) and (200) peaks of standard anatase TiO$_2$ phase (JCPDS card No. 21-1272) without any other impurities for both as-prepared and post-treated TiO$_2$ nanobelts. No other phases such as rutile TiO$_2$ or Na$_2$Ti$_3$O$_7$ are detectable. These results indicate that the surface modifications do not destroy the composition and nature of the materials. After the growth of MoS$_2$, additional peaks at 14.38°, 33.40° and 58.90° show up which are assigned to (002), (100) and (110) diffraction patterns in hexagonal phase MoS$_2$ (a = b = 0.316 nm, c = 1.230 nm, JCPDS card No. 37-1492) [32]. The TiO$_2$ diffraction peaks remain sharp after the formation of MoS$_2$/TiO$_2$ hybrid complexes suggesting good crystalline of TiO$_2$. By calculating the full width at half maximum (FWHM) value of the (002) diffraction peak using Scherrer equation, the thickness of MoS$_2$ sheet along the c axis was estimated to be 7.2 nm, or ~10 layers.

The morphology and size of TiO$_2$ nanobelts are characterized by SEM, which reveals the difference for various treatments. Figure 2(a) presents SEM image of the as-prepared TiO$_2$ nanobelts, which are about 50-70 nm thick and several micrometers long. The surface of the as-prepared TiO$_2$ nanobelts is smooth and uniform. Therefore, MoS$_2$ can barely grow on the untreated TiO$_2$ surface. In a separated experiment, our method can prepare nicely ordered MoS$_2$ flower, as shown in Figure 2(b). In Figure 2(c), 2(e) and 2(g), the SEM images of post-treated TiO$_2$ nanobelts are given as well as their composites with MoS$_2$ in Figure 2(d), 2(f) and 2(h). The geometry structure of the post-treated TiO$_2$ nanobelts is more or less the same after different surface etching treatments. After the surface etching treatment, the TiO$_2$ nanobelts were cracked into thicker (60-200 nm) and rougher ones. However, their surface roughness is strongly modified upon different acid and base treatments. From Figure 2, one can see that H$_2$SO$_4$ treatment exhibits more influence on the surface morphologies. For the samples experienced H$_2$SO$_4$ treatments, see Figure 2(e), their surfaces become rough and decorated. In Figure 2(f), there exists some small particles and porous features evenly distributed on the surface of nanobelts, which is consistent with previous observations [33]. The surface modification of TiO$_2$ provides more nucleation sites for the growth of MoS$_2$ nanosheets.
As shown clearly, the surface engineering can create more nucleation sites which (1) provides more adsorption sites for MoS$_2$ to land on; (2) facilitates the formation of defect-rich MoS$_2$ structures. Therefore, it is expected that MoS$_2$ nanostructures grown on these treated TiO$_2$ nanobelts would favor the HER electrochemical catalysis. One should note that although the SEM image of TiO$_2$-NH shows smoother surface, its surface nucleation sites has already formed at nanoscale which will be discussed later. In general, both acid or base treatment results in the formation of dangling bond for the growth of MoS$_2$ [34]. In comparison, NaOH/HCl can rough the surface in nanoscale while H$_2$SO$_4$ solution peels off the surface structure to form microscale structures. As shown, the surface morphologies of different post-treated TiO$_2$ nanobelts are strongly distinguishable which are expected to exhibit different catalytic performance for their MoS$_2$/TiO$_2$ hybrid complexes. Either the base or acid treatments leads to the formation of dangling bond acting as growth nucleation sites.

Bright field cross-section TEM images are given in Figure 3 for MoS$_2$/TiO$_2$ hybrid heterostructures with different post-treated interfaces, where both MoS$_2$ nanoflowers and nanosheets can be observed to decorate the surface of TiO$_2$ nanobelts. As shown in Figure 3, the TiO$_2$ nanobelts penetrate through MoS$_2$ nanoflowers regardless of the surface post-treatment methods. The surface of modified TiO$_2$-NH nanobelts are relatively smoother while H$_2$SO$_4$-treated surface possesses more particle and pore features, which is consistent with the SEM results. The lateral size of MoS$_2$ sheets is about 100 nm and they are suspended vertically on TiO$_2$ nanobelts which can expose high density of active sites. As shown, the MoS$_2$ sheets are transparent, frizzle and flexible, demonstrating their ultrathin and layered structure [34]. Indeed, the modification of TiO$_2$ surface leads to the growth defects of MoS$_2$. Many reports demonstrated that the defect-rich samples show more active edges and exhibit higher catalytic activity [28-31]. It is clearly indicated that there are more particles features on TiO$_2$-NHH than others. In Figure 3(b), 3(d) and 3(f), for different post-treatments, the affected surface layer thickness are 16 nm, 10 nm and 7 nm, for TiO$_2$-NH, TiO$_2$-NHH, and TiO$_2$-H surfaces, respectively. This implies the function of H$_2$SO$_4$ is to peel off some surface structure as agreed with above SEM observations.

XPS was used to investigate the interface chemistry as well as the electronic structure of the synthesized heterostructures. The valence band of MoS$_2$ is built up by the hybridization of Mo 4$d$ and S 3$p$, which exhibits four major features within 0–10 eV. As shown in Figure 4, the electronic states of Mo 4 band is readily developed at ~2 eV. The higher binding energy Mo 4$d$ - S 3$p$ orbitals are overlapped with the substrate O 2$p$ peaks. These observations indicate well-developed bands formation from hybridized Mo 4$d$ - S 3$p$ orbitals, which implies long-range in-plane ordering of the MoS$_2$ structure. The core level spectra of Ti 2$p$ peak from TiO$_2$ substrate can be used as reference to align the valence band and core level spectra with/without MoS$_2$ overlayers to determine the value of valence band offset at the MoS$_2$/TiO$_2$ interface. As shown in Figure 4(a), the leading edge of the valence band of bare TiO$_2$...
substrate and MoS$_2$/TiO$_2$-NH were determined to be $2.53 \pm 0.05$ eV and $0.17 \pm 0.05$ eV, respectively, by the intersection of the regression determined line segments defining the edge and the flat energy distribution curve in the energy gap region. Therefore, the valence band edge difference with and without MoS$_2$ is used for determining the valence band offset (VBO) of MoS$_2$/TiO$_2$ system after aligning the Ti 2$p$ peak position for both systems. Since the band gap of MoS$_2$ is $\sim 1.2$ eV, the conduction band offset (CBO) at MoS$_2$/TiO$_2$ interface can be estimated. Applying the same method, VBO and CBO for TiO$_2$-NH and TiO$_2$-H can also be determined.

The VBO and CBO information is schematically given in Figure 4(d). As shown clearly, type II band alignments are formed for all post-treated samples. In Figure 4(d), the VBO(CBO) gradually increases from $2.41(0.39)$ to $2.69(0.71)$ eV for TiO$_2$-NH, TiO$_2$-NH and TiO$_2$-H surfaces, respectively. This indicates that surface treatments play important roles to the interface electronic behaviors. As shown, when the surface is treated by H$_2$SO$_4$, the VBO increases due to the interface states. The change of VBO(CBO) can be partially due to the electron redistribution on the post-treated surfaces. Another reason is attributed to the interface interaction between MoS$_2$ and TiO$_2$ which puts the MoS$_2$ bands at different energy level. This difference should affect their interface charge transport properties and thus the photocatalytic behaviors.

For $\text{H}_2\text{SO}_4$-treated surface, both VBO and CBO are the largest, the electrons and holes thus have largest possibility to separate. Therefore, its photocatalytic activities should be the best. In Figure 5, the photocatalytic activity measurements are presented. Our photocatalytic activity measurements show that MoS$_2$/TiO$_2$-H exhibits the best photocatalytic activity as compared to MoS$_2$/TiO$_2$-NH and MoS$_2$/TiO$_2$-NH, which is in line with our band alignment arguments. Our results emphasize the importance of the interfacial engineering for the photocatalytic activities of MoS$_2$/TiO$_2$ composites. The superior photocatalytic activity of MoS$_2$/TiO$_2$-H could also be related to its more oxidized interface which leaves minimal recombination centers.

The electrocatalytic performance was investigated using linear scan voltammetry in 0.5 M H$_2$SO$_4$ solution for the same amount of MoS$_2$/TiO$_2$ catalysts loaded on glassy carbon (GC) electrode (loading: ca. 0.285 mg/cm$^2$). In general, higher acid

![Figure 4](image-url)  
**Figure 4.** Comparison of valence band of TiO$_2$ nanobelts (black curve) and that after MoS$_2$ growth (red curve). (a) for TiO$_2$-NH, (b) for TiO$_2$-NH and (c) for TiO$_2$-H. (d) Schematic diagram of band alignment for MoS$_2$/TiO$_2$ heterostructures with different surface treatments.

![Figure 5](image-url)  
**Figure 5.** The photocatalytic performance of MoS$_2$/TiO$_2$ heterostructure. (a) MoS$_2$/TiO$_2$-NH (b) MoS$_2$/TiO$_2$-NH (c) MoS$_2$/TiO$_2$-H. The degradation rate is given in (d).
The HER mechanism for MoS2 still remains inconclusive, while we can speculate the reaction based on the Tafel slope. In fact, it is more impressive that the Tafel slope of MoS2/TiO2-H is greatly reduced from 140.7 mV/dec to 66.9 mV/dec, which is well below that of 95 mV/dec reported for MoS2 nanoflakes on conductive substrate, PyC [26], and close to the so-far best reported value, ~40 mV/dec [37]. The determination and interpretation of the Tafel slope are important for the elucidation of the elementary steps involved. The observed Tafel slope of 66.9 mV/dec in current work suggests increased accessible sites for hydrogen adsorption as is consisted with the Volmer-Heyrovsky mechanism put forward by Li et al. [37]. As shown in SEM, the amount of surface defective features follow the trend of TiO2-NH < TiO2-NHH < TiO2-H, which is the same as the HER activities of their corresponding complexes. This indicates that the interface properties of MoS2/TiO2 are important in improving their catalytic activity. Our results show a steady decrease of Tafel slope for H2SO4-treated samples. This is likely attributed to the fact that H2SO4 creates greater density of defective sites, as observed in SEM measurements, which in turn provides a greater number of accessible sites for H_ads.

It was reported that the effective electronic coupling between the oxide and MoS2 can also enhance the HER performance [26]. Our TEM measurements show that MoS2 can strongly chemically bonded with TiO2. This intimate chemical bonding ensures the effective electronic coupling needed for high HER performance. Moreover, the trend of HER activities is consistent with our band structure alignment measurements where the MoS2/TiO2-H has the largest band offset warranting fast charge transport across the interface. As reported, the H2SO4 modified decreased the work function of TiO2 [38]. This could also be accounted for the change of CBO. The improved HER activity should be strongly correlated to the fast electron transfer at the intimately bonded MoS2/TiO2 interface, which is favored by the largest CBO for MoS2/TiO2-H where stronger build-in electric field is introduced. This is also confirmed by the electrochemical impedance measurement. As shown in Figure 7, the comparison of Nyquist plots between MoS2 and MoS2/TiO2-H is given at the over-potential of 270 mV. As shown, in the same condition, the MoS2/TiO2-H complex exhibits a smaller charge transfer resistance (Rct, about 80 Ω vs. 12 kΩ). The small Rct warrants fast charge transfer at the interface, thus better electro-catalytic performance.

CONCLUSION

In summary, three different post-treated TiO2 nanobelts are prepared which all lead to strong chemical coupling of MoS2 with TiO2 although the nucleation sites are different. Type II band alignment is established for all samples. However, varied surface treatments play significant roles on the surface electron distribution at the interface which controls their band
alignment. This band structure information can be used to explain their photocatalytic behaviors. The interface engineering shows important roles for HER with the MoS$_2$/TiO$_2$-H sample exhibiting the best performance. The high HER activity can be attributed to the synergistic effect of the defect-rich MoS$_2$, effective electronic coupled interface as well as the interfacial build-in electric field for fast electron transfer.

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Notes

The authors declare no competing financial interest.

References


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