

Research Article

Investigating Visible-Photocatalytic Activity of MoS₂/TiO₂ Heterostructure Thin Films at Various MoS₂ Deposition Times

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MoS₂/TiO₂ heterostructure thin films were fabricated by sol-gel and chemical bath deposition methods. Crystal structure, surface morphology, chemical states of all elements, and optical property of the obtained thin films were characterized by using X-ray diffraction, scanning electron microscopy, X-ray photoelectron spectroscopy, and UV-Vis spectroscopy techniques, respectively. Photocatalytic activity of all thin films was evaluated by measuring decomposition rate of methylene blue solution under visible light irradiation. The results indicate that ultrathin MoS₂ film on TiO₂-glass substrate improves photocatalytic activity of TiO₂ in the visible light due to the efficient absorption of visible photon of MoS₂ few layers and the transfer of electrons from MoS₂ to TiO₂. All MoS₂/TiO₂ heterostructure thin films exhibit higher visible light photocatalytic activity than that of pure MoS₂ and TiO₂ counterparts. The best MoS₂/TiO₂ heterostructure thin film at MoS₂ layer deposition time of 45 minutes can decompose about 60% MB solution after 150 minutes under visible light irradiation. The mechanism of the enhancement for visible-photocatalytic activity of MoS₂/TiO₂ heterostructure thin film was also discussed.

1. Introduction

TiO₂ with a large band-gap semiconductor (3.0 eV for rutile and 3.2 eV for anatase) has been widely applied in solar energy conversion and environmental purification, such as TiO₂-based photocatalysts and dye-sensitized solar cells [1, 2]. However, due to its large band-gap, TiO₂ can only absorb ultraviolet (UV) light which accounts for only 5% of the solar energy, so some applications of TiO₂ have been limited to the ultraviolet light region [3]. Therefore, it is necessary to improve the photocatalytic activity of TiO₂ under visible light irradiation (~45% of sun energy).

There have been some approaches to be used to improve photocatalytic performance of TiO₂ under visible light, such as doping or semiconductor coupling (TiO₂-based heterostructures). Impurity doping is one of the typical approaches [4–8]. However, doping can usually cause high recombination rate and the low carries mobility of photoexcited electron-hole pairs and make TiO₂ thermally unstable [9].

Semiconductor coupling has been receiving much attention recently. By coupling between TiO₂ and a smaller band-gap semiconductor with matched edge-energy levels, electrons can transfer from semiconductor to TiO₂, which makes a shift of TiO₂'s photocatalytic activity from UV light to visible light. The prerequisite for these semiconductors is that their conduct band minimum has to be more positive than that of TiO₂ [10–12].

Recently, layered molybdenum disulfide (MoS₂) has attracted much attention due to its unique electrical and optical properties. Monolayer MoS₂ is a direct band-gap of 1.9 eV and multilayer/bulk MoS₂ is a 1.2 eV indirect band-gap [13]. The band-gap of MoS₂ ultrathin film matches the solar spectrum absorption closely and its stability against photo-corrosion [14]. Furthermore, the conduction band minimum of MoS₂ ultrathin film is higher than that of TiO₂, so in the heterostructure of MoS₂/TiO₂, electrons from excited band-gap of MoS₂ thin film can inject efficiently into TiO₂ under

visible light [15, 16]. Therefore, MoS₂ is considered either a photo-sensitizer for visible light or an electron transfer mediator in the heterogeneous semiconductor systems [17].

Until now, there have just been few reports on MoS₂/TiO₂ in composites, nanopowder or core-shell materials for photocatalytic performance under visible light. For example, Kanda et al. fabricated MoS₂/TiO₂ photocatalyst applied in hydrogen generation [16]. According to Zhou et al., the MoS₂/TiO₂ heterostructure with 50 wt% MoS₂ exhibits the highest hydrogen production [18]. Zhou et al. deposited MoS₂ thin film layer on TiO₂ nanotubes and the sample with 1 nm thickness of MoS₂ exhibited the strongest H₂ evolution activity [17]. Zhang et al. used mild impregnation method to assemble exfoliated MoS₂ shell on anatase TiO₂ mesocrystal; their photocatalyst had high H₂ evolution rate of 0.55 mmol h⁻¹ g⁻¹ and good reusability under UV light [19]. Zhang et al. employed ultrasonic-hydrothermal method to synthesize TiO₂/MoS₂@zeolite composite photocatalyst which highly enhanced photocatalytic activity for degradation of methyl orange under solar-light irradiation [20]. However, researches have been rarely studied for MoS₂/TiO₂ heterostructure thin film. The important advantages of photocatalytic thin film over powder are its reusability and recovery. In this study, we fabricated MoS₂/TiO₂ heterostructure thin film by sol-gel and chemical bath deposition methods. The relationship between physical properties and photocatalytic activity was discussed in detail. Methylene blue dye was selected as a model reactant for photodegradation.

2. Experiment

The MoS₂/TiO₂ (MT) heterostructure thin films were fabricated by a combination of sol-gel and chemical bath deposition methods.

First, TiO₂ thin films were prepared on glass substrates by using dip coating process. The details of the procedure for making the TiO₂ samples have been described in our previous work [21]. Tetrabutyl orthotitanate (Ti(OBu)₄) (99.99%) was dissolved in a mixture solution of diethanolamine (HN(C₂H₄OH)₂) (99.99%) and ethanol (C₂H₅OH) (99.99%). Then distilled water was added dropwise with continuous stirring for 2 hours to get TiO₂ sol solution. We used glass plates as the substrates which were dip-coated in the above sol to obtain TiO₂ films. These films were dried at 80°C for 15 minutes and were annealed at 500°C for 2 hours in the air.

Second, we synthesized MoS₂ ultrathin film on TiO₂ thin film via chemical bath deposition method. Thiourea (CS(NH₂)₂) and ammonium paramolybdate ((NH₄)₆Mo₇O₂₄·4H₂O) were alternately added to deionized water under continuous stirring for 90 minutes to form a homogeneous solution. In addition, hydrazine hydrate (35 wt%) was added to the above mixture solution with vigorous stirring for 10 minutes. Inside the chemical bath, we inserted glass substrate which was coated TiO₂ thin film to grow MoS₂ ultrathin film. This bath was kept at 80°C for different deposition time of MoS₂ layer (15, 30, 45, and 60 minutes). After chemical bath deposition process, the bath was cooled down to room temperature naturally. A MoS₂ ultrathin film was deposited onto TiO₂ thin film, which was

washed in the ultrasonic cleaner with distilled water to get rid of heterogeneities and then dried at room temperature. Finally, the obtained products were annealed at 500°C for 2 hours under continuous flow of nitrogen gas. The MT heterostructure thin films at various MoS₂ layer deposition times correspond to different thicknesses of MoS₂ films on the TiO₂-glass substrates.

All obtained samples include pure TiO₂ and series of MoS₂/TiO₂ heterostructure thin films at various MoS₂ layer deposition times of 15, 30, 45, and 60 minutes, which were labeled as TiO₂, MoS₂, MT15, MT30, MT45, and MT60, respectively. Pure MoS₂ sample at 45-minute deposition time and pure TiO₂ counterparts were prepared and denoted as MoS₂ and TiO₂ to compare with others.

The morphologies of samples were observed by scanning electron microscopy (SEM, Hitachi S-4800). Crystal structure of the samples was examined by X-ray diffraction (Bruker D8 Advance) using CuKα from 2θ = 10–70°. Optical absorption spectra of films were measured at room temperature in the air using a Halo RB-10 spectrophotometer. Degradation rate of methylene blue (MB) was measured to evaluate the photocatalytic activity of obtained thin films. Every 25 × 25 mm² film was dipped into 10 ml of 10 ppm MB solution with a pH of about 4.72. In the absence and presence of catalysts, MB solution was stored in dark for 30 minutes before irradiation to attain adsorption-desorption equilibrium. A compact light was used as a visible light source in this experiment. MB adsorptions at 662 nm were measured by a Halo RB-10 spectrophotometer at intervals of 30 minutes. We used Lambert-Beer's law to calculate the changes of MB concentration at regular irradiation intervals.

3. Results and Discussion

Figure 1 illustrates MB solution photodegradation by visible light irradiation catalyzed by TiO₂, MoS₂, and series of MT thin films at various MoS₂ layer deposition times. From Figure 1, it is clearly observed that TiO₂ thin film has a negligible MB photodegradation in visible light region, which can be originated from its UV light absorption. Meanwhile, we found that pure MoS₂ thin films have MB degradation of 30% within 150 minutes in visible light irradiation. This indicates that MoS₂ sample has a relatively low visible-photocatalytic activity which is explained by high recombination rate of electron-hole pairs. Furthermore, MT15 sample apart, the remaining MT thin films have higher photocatalytic performance in visible band compared with that of TiO₂ or MoS₂. This enhancement can be explained by the efficient visible light absorption of MoS₂ and the transfer of electrons from MoS₂ to TiO₂ in MoS₂/TiO₂ heterostructure thin films; from that, it decreases the recombination rate of electron-hole pairs and increases the photocatalytic activity in the visible light region.

In particular, photodegradation rates of MT15 and TiO₂ samples are relatively the same. This could be explained that MoS₂ layer did not exist on surface of MT15. According to Nair et al., in CBD procedure, there is a nucleation period which established various chemical equilibria to prepare for forming MoS₂ layer. Deposition time of 15 minutes is not

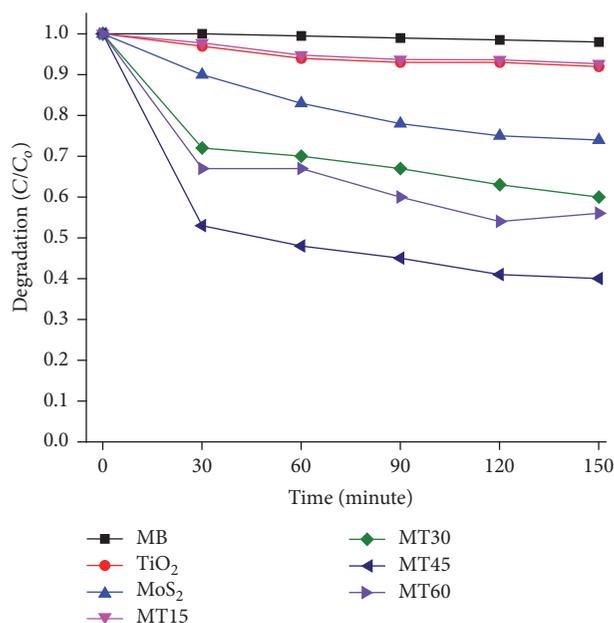


FIGURE 1: The photodegradation of MB solution for MoS₂, TiO₂, and series of MT thin films at different deposition time of MoS₂ under visible light irradiation.

long enough for growth of initial MoS₂ molecules [22]. Thus, it takes more than 15 minutes to form some early MoS₂ molecules on a surface of the substrate.

As demonstrated in Figure 1, MT45 exhibits the highest visible-photocatalytic activity compared to any of the remaining MT samples. Its degradation of MB solution reaches as high as 60% with 150 minutes. For MT30 sample, its thickness can be insufficient to absorb visible light. With MT60, the thickness is more. According to Nair et al. [22], following the nucleation period of CBD process, film growth rate is relatively large, and the number of monolayers of MT60 increases significantly. So its band-gap energy is reduced in which its conduction band bottom lies lower than that of TiO₂, which prevents photoexcited electrons from transferring to TiO₂ [14, 15]. In summary, MT45 sample has the highest visible-photocatalytic activity.

Figure 2 shows UV-Vis absorption spectra of TiO₂, MoS₂, and series of MT thin films. It can be seen that pure TiO₂ has an absorption edge of 380 nm corresponding to a band-gap energy of 3.2 eV, so TiO₂ is only active in UV light region. MoS₂ sample has strong absorption in visible light. Its band-gap energy was calculated from UV-Vis absorption spectrum using Tauc plot method and it was found to be approximately 1.87 eV as in the inset of Figure 2. After coating MoS₂ thin film onto TiO₂/glass substrates, all MT samples have an increase in the absorption of visible light except for MT15. This is attributed to narrow band-gap and dark color of MoS₂ nanosheets, which is beneficial to the visible-photocatalytic activity. In comparison with TiO₂, MT15 sample has relatively the same UV-Vis spectrum, so it confirmed that MoS₂ did not exist on its surface.

The XRD patterns of MoS₂, TiO₂, and MT45 sample are shown in Figure 3.

With pure TiO₂ thin film, diffraction peaks are observed at 25.2°, 37.8°, 48.1°, and 54.3° indexed as (101), (004), (200), and (211) plane lattices, assigned to the anatase phase of TiO₂, respectively [Anatase XRD JCPDS card number 78-2486].

As for pure MoS₂ sample, the two detected peaks at 2θ values of 14.4° and 32.7° can be assigned to the (002) and (100) planes of hexagonal phase MoS₂ ($a = b = 0.316$ nm, $c = 1.230$ nm, JCPDS card number 37-1492). The diffraction peak at 14.4° is corresponding to the c -plane of MoS₂ and can be used to study the structure of MoS₂, which is composed of Mo atoms coordinated with S atoms to form the S-Mo-S sandwich layer. The intensity of this peak is not high; it indicates that the MoS₂ nanosheets may have only few layers.

Interestingly, all of the diffraction peaks which are assigned for phases of TiO₂ and MoS₂ exist in XRD of MT45 sample. But the intensities of these diffraction peaks decrease and the peaks assigned to MoS₂ shift slightly to the right. These shifts could be the results from the distinct pressure stress on MoS₂ when MoS₂ nanosheets grow on TiO₂ thin film. So, it is said that TiO₂ might prevent the growth of MoS₂ crystals along the c -axis.

We estimated the thickness of the film with the SEM image taken in cross-section mode. Figure 4 shows the cross-sectional SEM image of MT45 sample. It is seen that the ultrathin MoS₂ layer is uniformly coated on TiO₂ thin film. The result exhibits the thicknesses of MoS₂ layer and MoS₂/TiO₂ thin films are approximately 12 nm and 245 nm, respectively. The 12 nm thickness of MoS₂ nanosheets could be the best appropriate thickness to cover on TiO₂ thin film and agrees with schematic illustration of charge-transfer of MoS₂/TiO₂ heterostructure thin film as followed.

X-ray photoelectron spectroscopy (XPS) is used to further clarify the structure of MT45 sample. As shown in Figure 5(a), the Mo⁴⁺ shows two peaks centered at 229 eV and 232 eV, attributing to the Mo 3d_{5/2} and Mo 3d_{3/2}, respectively. Furthermore, there is the small peak at 235.5 eV which indicates the residuals of Mo⁶⁺. For S 2p, there are two peaks consisting of S 2p_{3/2} and S 2p_{1/2} which are centered at 161.9 eV and 163.1 eV, respectively (as shown in Figure 5(b)). Two 2p_{3/2} and 2p_{1/2} peaks of Ti²⁺ were seen at 466 eV and 471 eV in Figure 5(c). The O 1s spectrum shows a peak at 537 eV in Figure 5(d). All the XPS positions of peaks are consistent with the reported values [19]. So there is the existence of Mo⁴⁺ (Mo 3d_{5/2} orbital and Mo 3d_{3/2} orbital), S²⁻ (S 2p_{3/2} orbital and S 2p_{1/2} orbital), Ti²⁺ (Ti 2p_{3/2} orbital and Ti 2p_{1/2}), and O²⁻ (O 1s orbital) in MT45 film. This result indicates that we have successfully fabricated the MoS₂/TiO₂ heterostructure thin film.

A schematic illustration for the photogenerated electron-hole separation and transfer process between MoS₂ and TiO₂ in TiO₂/MoS₂ heterostructure thin film is displayed in Figure 6.

The proposed mechanism for an enhanced photocatalytic activity in the TiO₂/MoS₂ heterostructure thin film under visible light irradiation assumes that the photoexcited electrons are transferred from the conduction band of MoS₂ thin film to the TiO₂ and eventually react with oxygen to produce superoxide anion radical [15]. Simultaneously, some

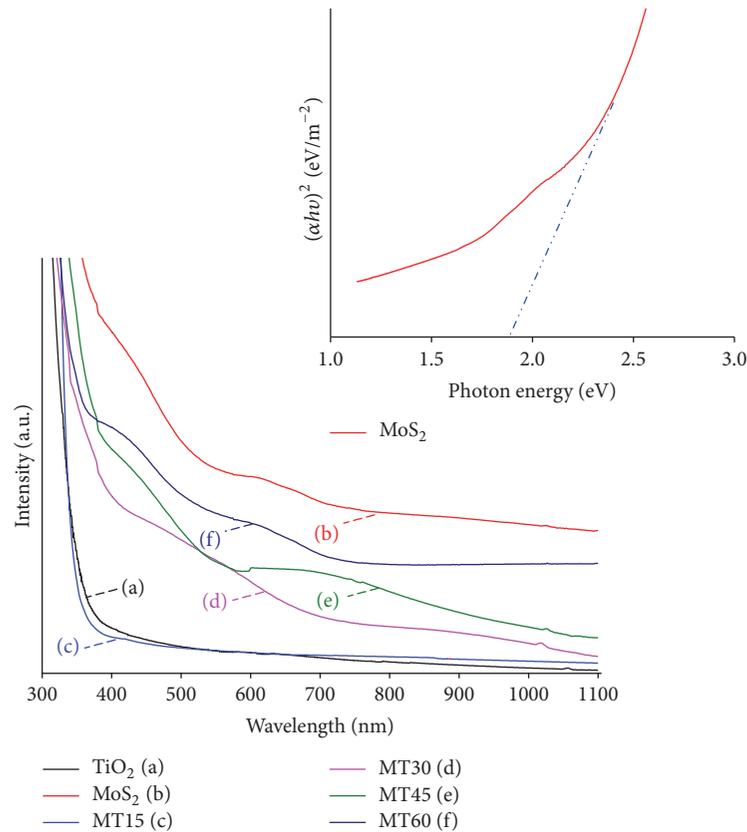


FIGURE 2: UV-visible absorption spectra of MoS₂, TiO₂, and series of MT thin films at different deposition time of MoS₂ under visible light irradiation. The inset of the figure: Tauc plot for MoS₂ thin film.

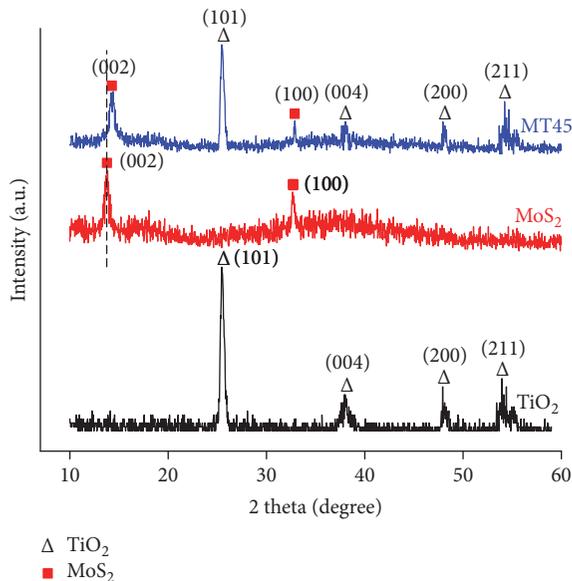


FIGURE 3: XRD pattern of pure MoS₂, pure TiO₂, and MT45 thin films.

holes move from the valence band of TiO₂ to the valence band of MoS₂ and MB solution is degraded. Consequently, MoS₂/TiO₂ heterostructure thin film can absorb visible light efficiently and supply more reaction active sites, leading to the superior photocatalytic activity.

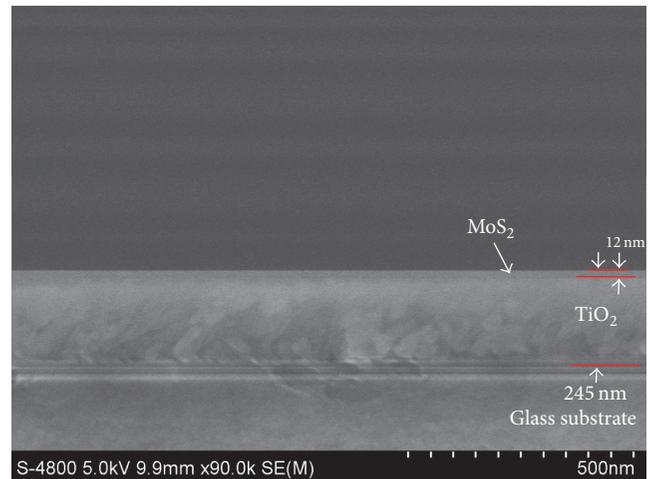


FIGURE 4: Cross-sectional SEM image of MT45 thin film.

4. Conclusion

MoS₂/TiO₂ heterostructure thin films have been successfully prepared by combination of sol-gel and chemical bath deposition methods. The results show that coating ultrathin onto TiO₂-glass substrate enhances photocatalytic activity under visible light. The mechanism for the improved photocatalytic activity in the MoS₂/TiO₂ heterostructure thin film

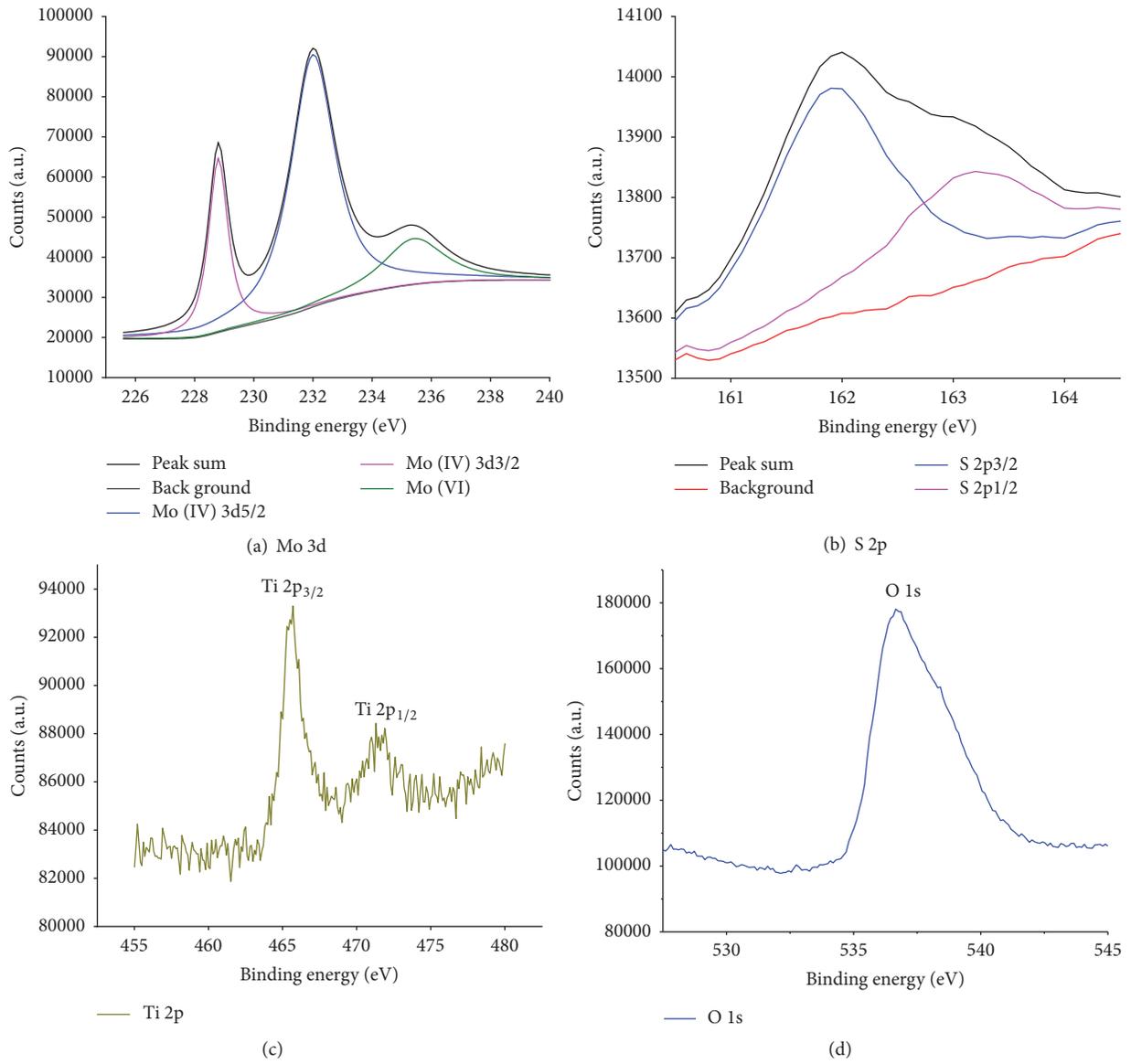


FIGURE 5: XPS spectra of MT45 thin film.

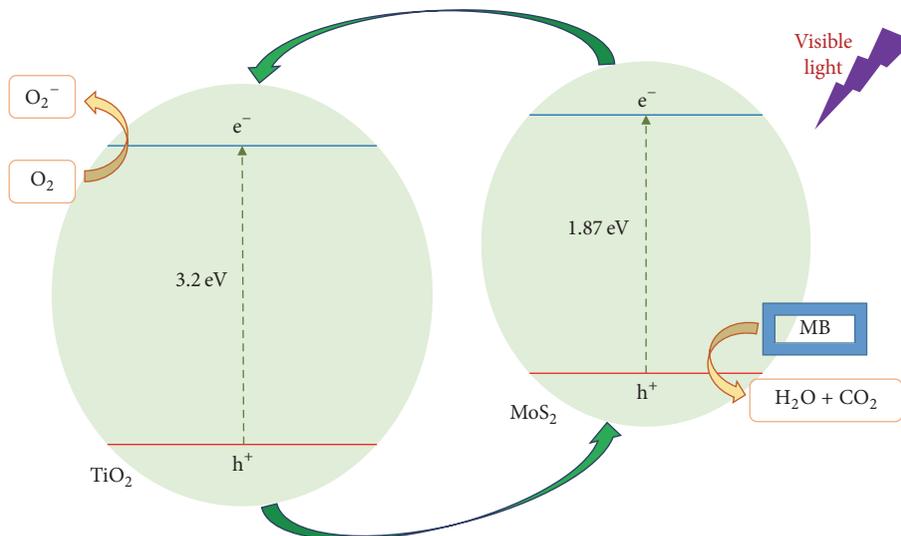


FIGURE 6: Schematic illustration of charge-transfer of MT heterostructure thin film for photocatalytic activity in the visible light.

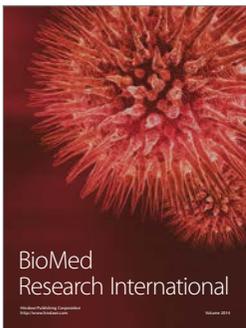
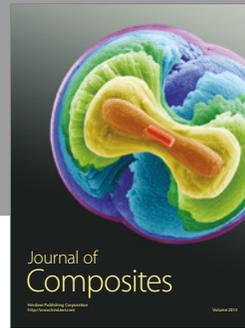
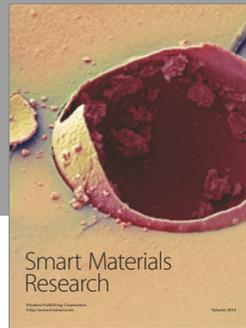
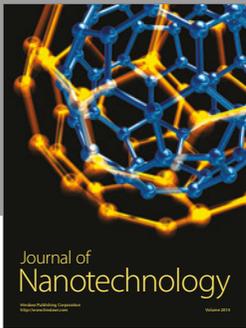
is discussed in detail. The MoS₂/TiO₂ heterostructure thin film at 45-minute deposition time of MoS₂ layer shows the best visible-photocatalytic activity with MB photodegradation rate about 60% after 150 minutes under compact light irradiation.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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