Effects the Surface of Solar-light Photocatalytic Activity of Ag-doped TiO2 Nanohybrid Material prepared with a Novel Approach

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Abstract

Surface modification with a nanomaterial has been confirmed to be an effective strategy to enhance the visible-light photodegradation efficiency of titanium dioxide nanoparticles (TiO_2-NPs). In this regard, we used silver as an additive into TiO2-NPs to improve their photodegradation activity under visible light irradiation. Herein, a novel and eco-friendly process was developed to prepare the Ag-doped TiO_2 nanohybrid and named as photon-induced method (PIM). The XRD technique showed that the prepared Ag-doped TiO_2 has mixed phases of anatase and rutile. However, the rutile-only phase was detected for the pure TiO_2-NPs at 700°C of calcination. Ultraviolet-visible (UV-vis) absorption spectra revealed a reduction in the bandgap energy of TiO_2 after Ag doping. Besides, the addition of Ag resulted in a significant improvement of TiO_2 morphology. Methlyene blue (MB) dye was chosen to be an organic target to investigate the photocatalyst activity of the TiO_2-NPs. In this regard, the degradation rate of MB was found to be 100% for the Ag-doped TiO_2, which is higher than that of pure rutile TiO_2. The incorporation of Ag additive plays a significant role in the improvement of TiO_2 stability and photodegradation performance due to the surface plasmon resonance phenomenon.

Introduction

Nowadays, nanomaterials (NMs) are an important type of advancing structure and attract great attention from research society and industries. Semiconductor NMs such as TiO_2, zinc oxide, tin oxide, and so on are the most used materials for various applications due to their fascinating features [1–3]. Also, nanoparticles have been prepared and employed in last decades due to their size-hooked on chemical and physical properties [4–6]. The use of NM for biomedical applications are crucial because NMs tend to be at the lowest level and immediately permit the food chain of the ecosystem [7]. Recently, researchers draw superior interest to TiO_2 and silver (Ag) incorporated TiO_2 crystalline structure because of their excellent electrical, optical, and chemical characteristics [8–10]. The semiconducting TiO_2 has an incredible photodegradation performance, which is mainly used as a photocatalyst due to its high light sensitivity, low environmental impact, strong oxidizing power, chemical inertness, and relative cheapness [11]. In addition, TiO_2 can be employed as an antimicrobial agent to deactivate microorganisms because of its chemical and physical stability, good photocatalytic efficiency, and ease of fabrication [12]. Nevertheless, two drawbacks limit the use of TiO_2, which are low absorption ability in the visible range can be absorbed only under UV light and high recombination of carrier charges [13].

A broad variety of noble metals may well be combined with the TiO_2-NPs to prompt photodegradation performance of dyes under visible light [14]. To date, Ag is an inexpensive metal with unique electronic merits compared with other ones, which makes it a good candidate for employing as an additive into the TiO_2-NPs [15]. Thus, Ag can impede the recombination rate of the carrier charges by receiving the TiO_2 photo-induced charge, which serves as an electron accumulator [16]. Moreover, the wide bandgap energy of TiO_2 can be easily tuned by Ag modification leading to increasing the absorption of visible light [17].

To increase the photodegradation performance, several interdisciplinary studies have been conducted on TiO_2 [18–20]. As reported in the literature, photocatalytic performance of NMs depends upon their crystallinity [21], additive engineering [22], surface area, and hydroxyl group [23]. Besides, Ag incorporating on the surface of semiconductors used to improve the photocatalytic performance by slowing down recombination rates [24]. Lin and coworkers prepared mesoporous TiO_2 doped with Ag^+-coated graphene (MT-Ag/GR) by a sol–gel and solvothermal methods as catalyst. The as-prepared hybrid of MT-Ag/GR showed stronger photodegradation abilities of MB dye than those realized with pure MT, MT-Ag, and MT/GR [25]. Siti and coworkers reported the development of a two-dimensional and porous metals-doped TiO_2 hybrids for studying their photocatalytic activity. They revealed that the Ag additive enhances the crystalline structure and gives an external oxidation level into the system for an improved charge transport pathway and surface reaction. As a result, this hybrid structure enhanced the photocatalytic activity toward rhodamine B [26]. Recently, our group investigated the visible-light photocatalytic activity of pure TiO_2 prepared with facile and green process named as photo-induced method (PIM). Our previous findings showed that pure, highly crystalline, and good TiO_2-NPs catalyst can be achieved by suggested approach [27].

For further improvement of TiO_2 photodegradation efficiency, we used Ag additive TiO_2 and doped into TiO_2 lattice using PIM. The prepared hybrid was systematically compared with standard TiO_2 using a series of techniques. Most importantly, the photocatalyst activity of the prepared hybrid was measured by the photodegradation of MB organic under visible light irradiation.

Experimental Procedures

Synthesis of Ag-doped TiO_2

Briefly, 0.5 gm of silver nitrate ($AgNO_3$, Merck) and 3 gm of titanium tetra isopropoxide (TTIP, Sigma-Aldrich) were added to 1 L of distilled water. After that, the mixed solution was carefully stirred under a halogen light for 5 days. Then, the mixture was dried at 100 ^oC for 12 h and sintered at 700 °C for 60 min. The standard TiO_2 (Merck) sample was purchased and sintered at 700 °C for 60 min.

Photocatalyst activity

The photocatalytic performance of pure and Ag-doped TiO_2 nanohybrid was characterized using methylene blue degradation assay. An aqueous dispersion of MB (1×10^{-5} M) was stirred well with 0.05 g catalyst into a beaker containing 100 ml of deionized water. The obtained solution was maintained under sunlight for measuring the photodegradation activity. Finally, the absorption spectrum was measured at intervals of 5 min.

Characterization

UV-vis spectroscopy was used to record the optical characteristics of films using Ocean Optics. The structural properties of samples were conducted using the XRD technique (Shimadzu). The morphology of samples was investigated using field emission SEM (Mira3). Fourier transform infrared (FTIR) spectra of samples were obtained using a Burker device.

Results And Discussion

To characterize the crystal nature of standard and Ag-doped TiO_2 NPs, XRD measurement was performed in the range of 10°–75° (**Figure 1**). The XRD shows the patterns of TiO_2 and Ag-doped TiO_2 NPs after sintering at 700 ^{o}C for 60 min. The X-ray pattern of the Ag-TiO_2 hybrid matches with the standard TiO_2 without any X-ray peaks from the Ag dopant (JCPDS card no. 21–1272) [8]. Therefore, implying that the Ag additives are well loaded into the TiO_2 lattice [11]. The X-ray pattern of Ag-doped TiO_2 NPs shows a mixed phase of an anatase and rutile phase, while the standard TiO_2 shows rutile-only phase. The average crystallite sizes of the standard TiO_2 and Ag-doped TiO_2 were found to be 60 nm and 25 nm, respectively, as determined by the Scherrer formula [28–30]. Also, XRD clearly exhibits TiO_2 peaks without any related pattern corresponding to Ag.

The absorption spectra of pure and Ag/TiO_2 hybrid were recorded using a UV-vis spectrophotometer and are displayed in **Figure 2a**. As shown, the absorption spectrum of the hybrid sample reveals a redshift at the absorption edge may be ascribed from Ag addition. The bandgap energy of NPs was estimated by employing Tauc plot [31]. The plots of $(\alpha h\nu)^{1/2}$ vs energy ($h\nu$) are demonstrated in **Figure 2b**. The bandgap can be directly obtained via extrapolating the line to the x-axis intercept. In this content, the bandgap energy of pure TiO_2 was 2.87 eV, while Ag-doped TiO_2 decreased to 2.7 eV. For hybrid NPs. This red shifting indicates the suppression of the recombination process of carrier charge and consequently enhanced visible light absorbance [4].

To further explore the impact of Ag doping on the structural properties of the prepared TiO_2 NPs, FTIR analysis was studied. The FTIR spectra of standard and Ag-doped TiO_2 samples are illustrated in **Figure 3**. As shown, the peaks observed at ∼3426 cm^{-1} are assigned to the O-H vibration of the hydroxyl oxygen group [3]. By comparing with previous studies, the intensive peaks in the range of 744–726 cm^{-1} are corresponding to lattice vibrations of Ti–O–Ti bonds [10,12], which further confirms that the Ag additive is dispersed well into the TiO_2 lattice.

The FESEM micrographs of standard and Ag/TiO_2 NPs are depicted in **Figure 4**. In the pure TiO_2 NPs, the NPs seem to be more aggregated as revealed in **Figure a-c**. Comparing with pure TiO_2, this finding indicates that the shape and morphology of TiO_2 NPs change with Ag addition. The effect of Ag incorporating on the morphology TiO_2 is particles like structures, as shown in **Figure d-f**. Moreover, the FESEM observations demonstrate that the adding of Ag clearly altered in the morphology of the photocatalyst surface. The spongy and porous structure causes more surface area at high hardness that surely would be more effective for enhancing the light absorbance and photodegradation performance [32].

The Photocatalyst performance was estimated using the UV-vis measurements of MB degradation under visible light illumination. The NPs precursor is mixed with organic MB to form a colloidal solution using stirring for 5 min in the dark conditions. Then, the mixed solution containing NPs and MB was irradiated by solar light. Nevertheless, if the electrons and holes pass through the surface of the TiO_2 without recombination, they can act a part in different oxidation and reduction reactions with adsorbed agents, for example organic species, oxygen, and water. As shown in **Figure 5**, The electrons in the valence band can be energized to the conduction band, leaving a positive hole in the valence band of the photocatalyst. When a photocatalyst is illuminated by light with energy as the same to or greater than the bandgap energy, photocatalysis is initiated by electron-doping with Ag does not disturb the crystal structure of anatase TiO_2. The small size of Ag-TiO_2 hybrid increased surface area as indicated by the FESEM measurements, which an increasing lifetime of photogenerated electrons and holes. This process is beneficial to enhance the photocatalytic efficiency. Through measuring of the rate constants, the Ag-doped TiO_2 show to be markedly enhanced compared with standard TiO_2 sample. This is because of the small crystallite size of Ag-doped TiO_2 and suppressed recombination of charge pairs, and bandgap narrowing [33,34].

The photocatalytic activities of standard TiO_2 and Ag-TiO_2 hybrid calcined at 700 ºC are presented in **Figure 6**. In comparison, the photodegradation curves of MB by Ag-TiO_2 sample is 100% obtained within 30 min, whereas the standard TiO_2 sample, only 10% degradation of MB is achieved within 30 min (standard TiO_2 rutile phase only and large particle size so no photocatalytic activity). Thus, we find that Ag-TiO_2 sample shows enhanced degradation in this case. This may be correlated with the size of the particles, and mixed-phase and the bandgap.

Conclusion

In summary, Ag-doped TiO_2 hybrid with improved photocatalytic activity was obtained employing the photon-induced method, followed by light treatment. The oxidized Ag species are photo-chemically reduced to Ag particle, resulting in an enhancement of light absorption in the visible region associated with plasmonic absorption bands. With this treatment method, high-quality TiO_2 NPs prepared with higher crystallinity and better morphology compared with pure TiO_2. The results indicate that the enhancement of photodegradation activity was acquired after Ag doping. The result showed that the Ag-doped TiO_2 NPs had better photocatalytic activity than standard TiO_2.

Declarations

Conflict and Interest

The authors declare there is no conflict interest in this research paper.

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Figures

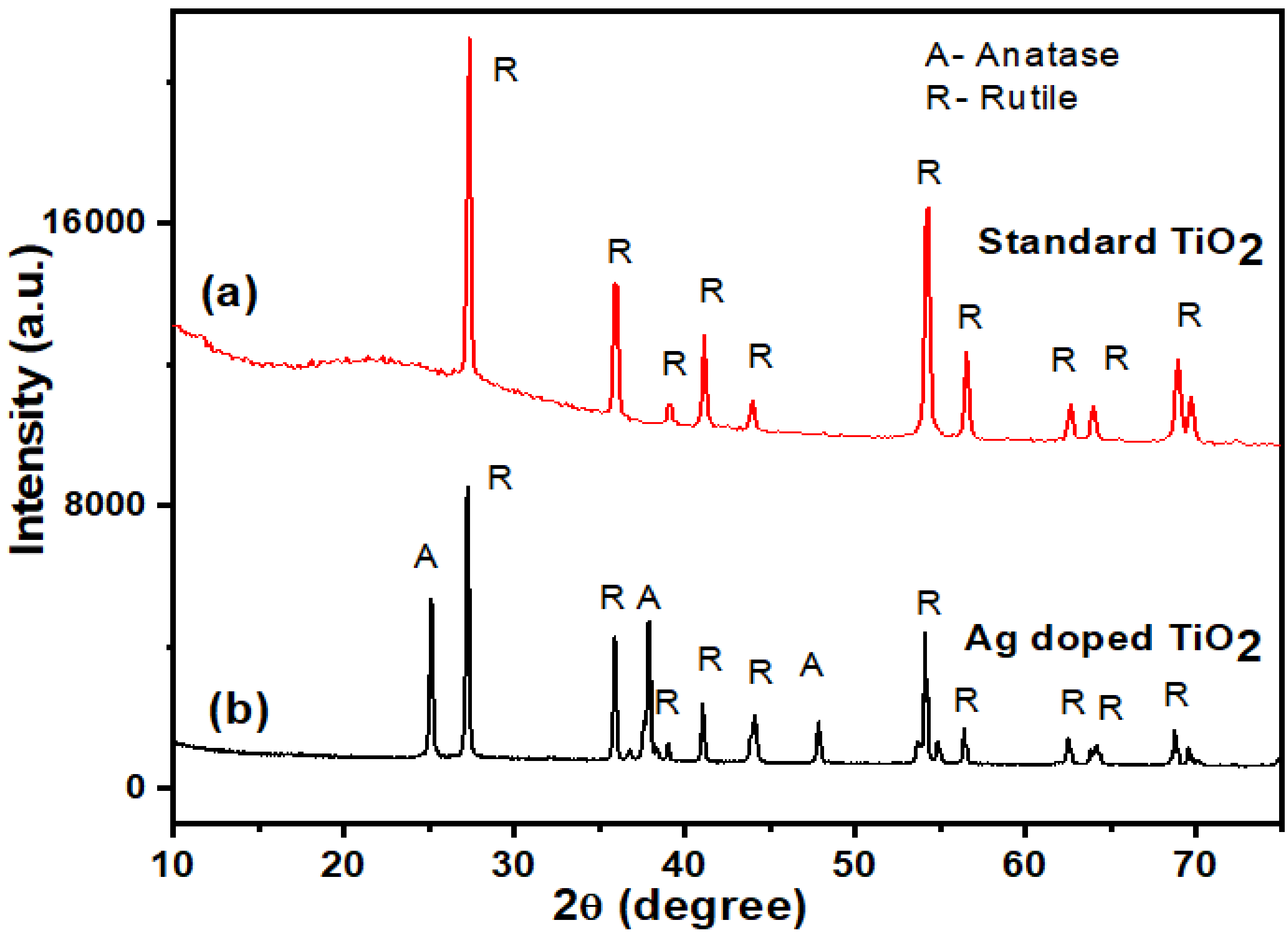
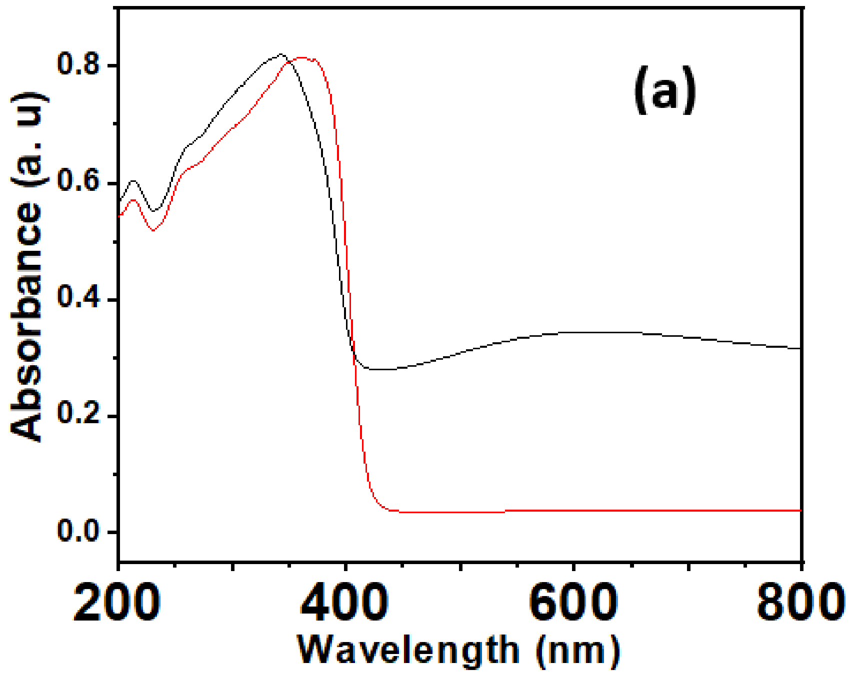


Figure 1

XRD patterns of a) pure TiO2, b) Ag-doped TiO2 NPs. A and R denoted to anatase and rutile phases, respectively.



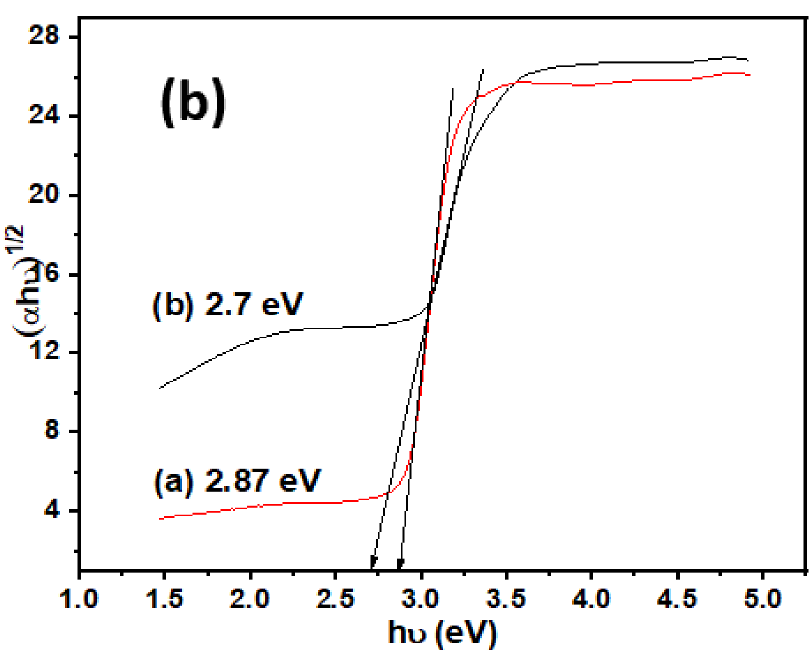


Figure 2

UV−vis a) absorbance and b) Tauc plot of pure and Ag-doped TiO2 NPs. Black and red lines are for TiO2 and Ag/TiO2, respectively.

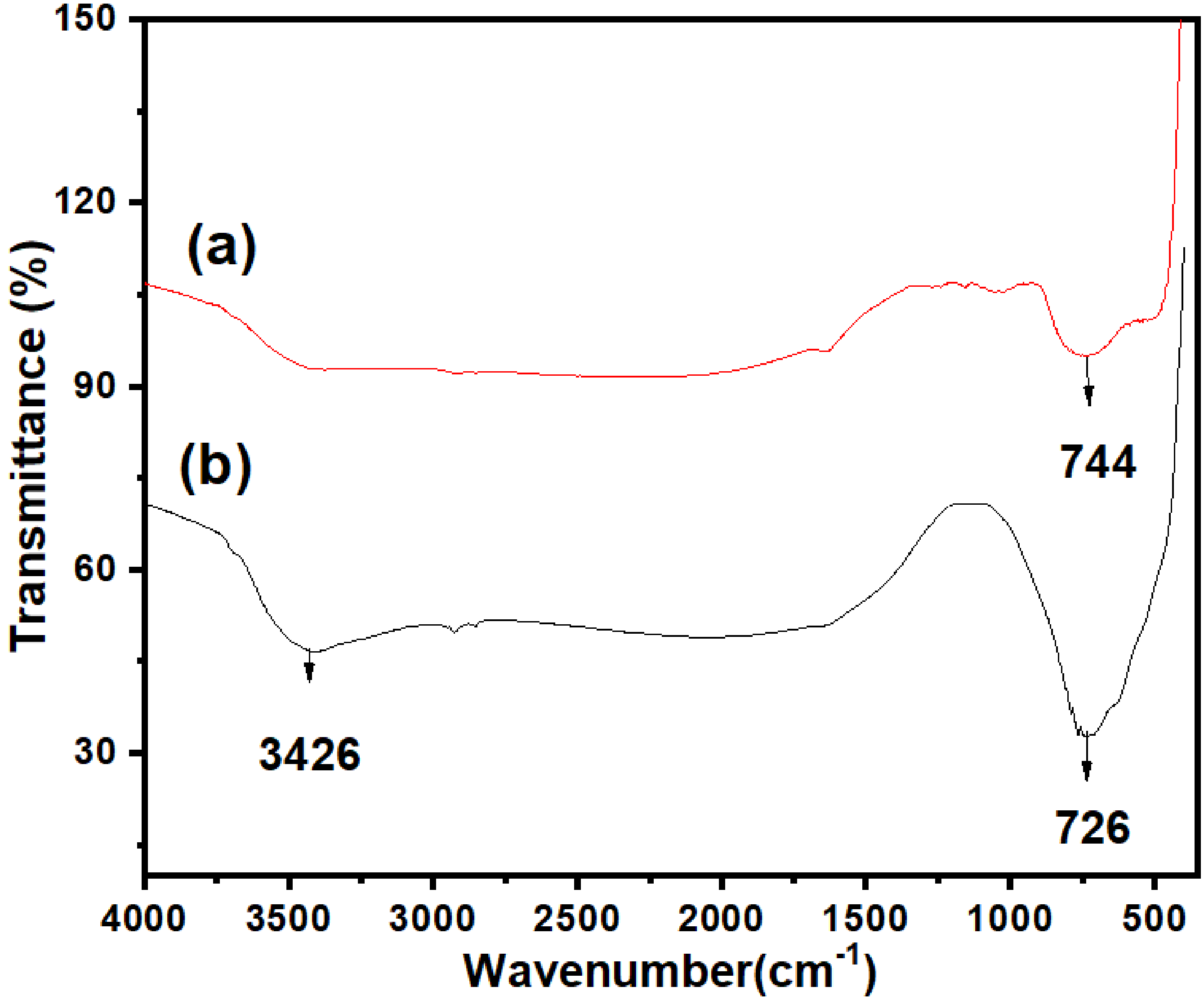


Figure 3

FTIR spectra of (a) pure TiO2 and (b) Ag-doped TiO2 NPs.

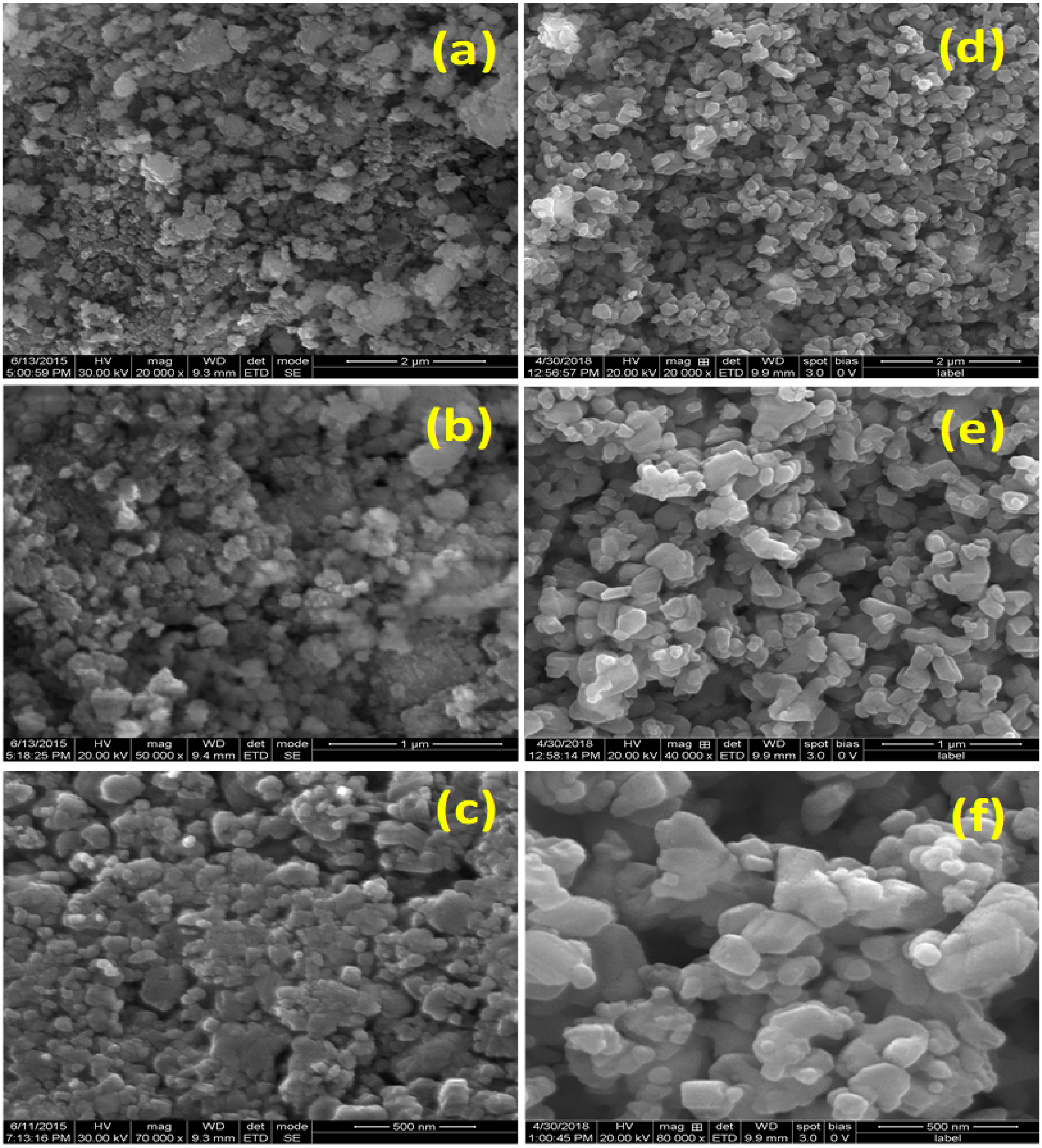


Figure 4

FESEM images of low and high magnifications of (a, b, c) pure and (d, e, f) Ag-TiO2.

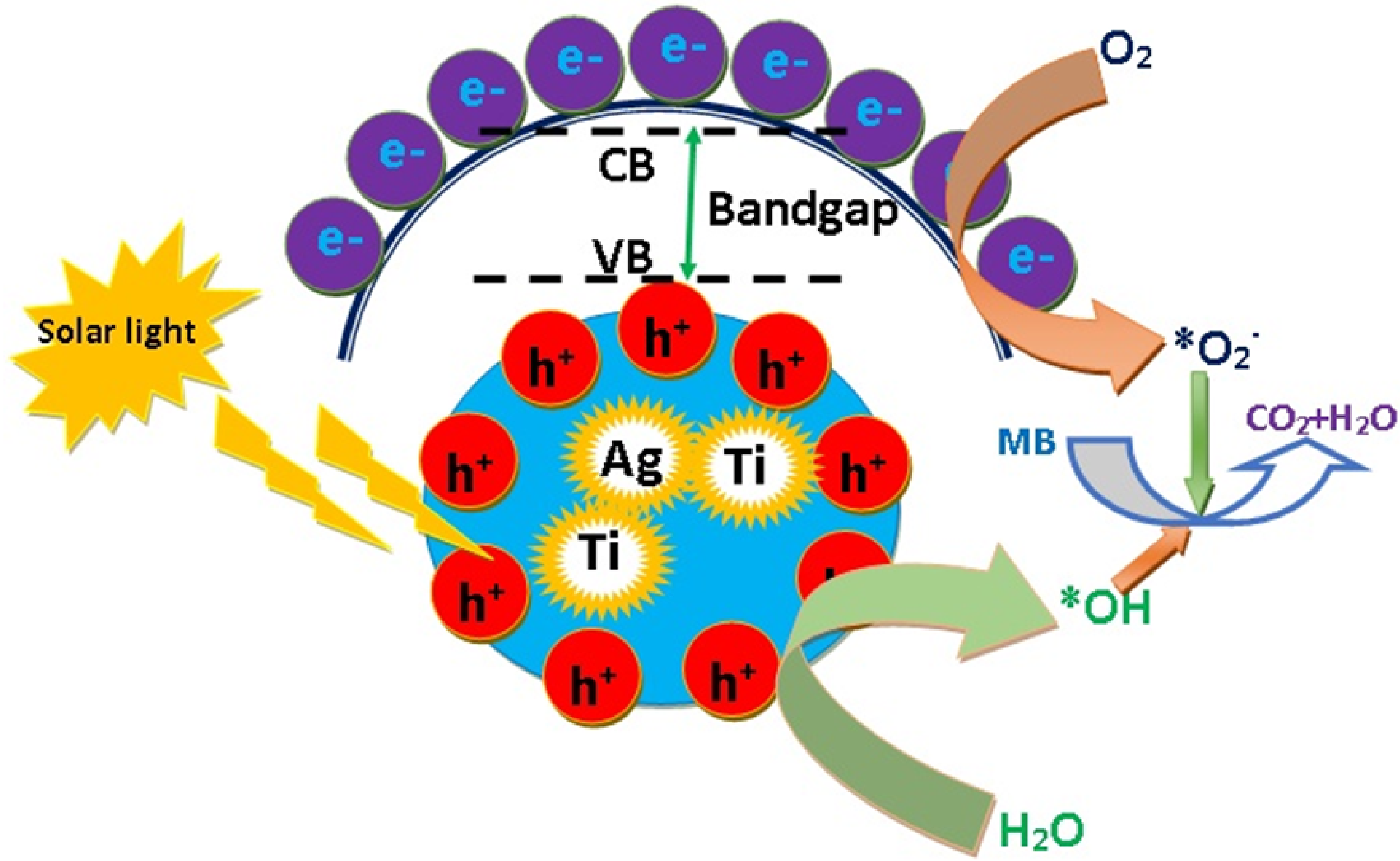
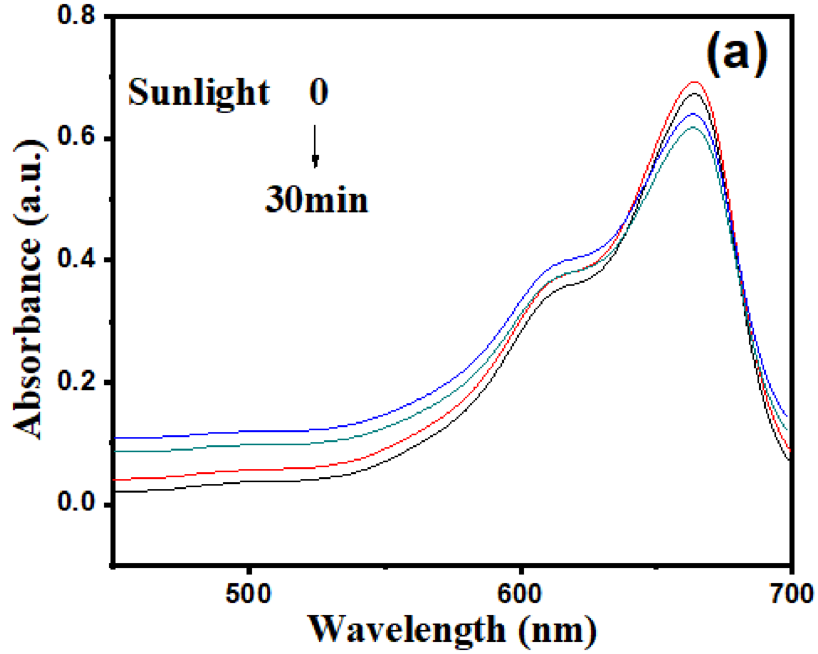


Figure 5

Photocatalysis mechanism of the prepared Ag/TiO2 hybrid.



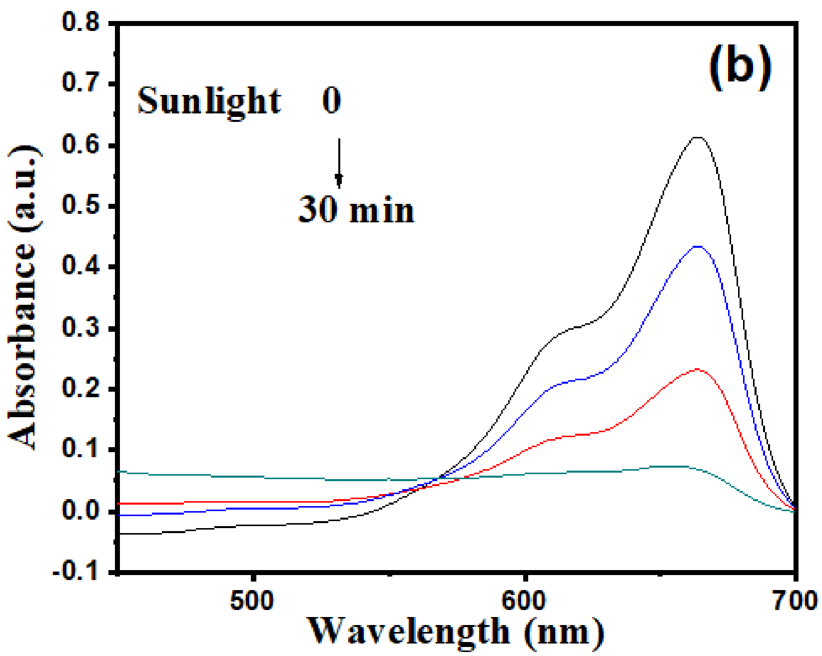


Figure 6

(a) MB dye by standard TiO2 under solar-light, (b) MB dye by Ag-TiO2 under solar-light.