



Evaluation of Ag@TiO₂/WO₃ heterojunction photocatalyst for enhanced photocatalytic activity towards methylene blue degradation

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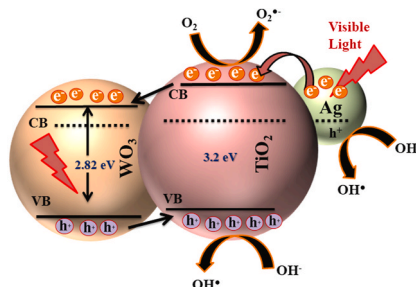
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HIGHLIGHTS

- Heterojunction Ag@TiO₂/WO₃ nanocomposite was synthesized.
- This novel nanocomposite design resulted in high degradation of MB.
- The synergistic effect of SPR and metal-oxide enhanced photocatalytic activity.
- A higher degradation rate is achieved compared to the pristine counterparts.

GRAPHICAL ABSTRACT



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ABSTRACT

Methylene blue is a dye that is extensively used in the textile industry but it is a hazardous, carcinogenic, and mutagenic pollutant. Therefore, the treatment of wastewater containing methylene blue by photocatalytic degradation under visible light without using any sacrificial agent (H₂O₂) is an important method towards attaining an eco-friendly environment. Herein, the nanocomposite of Ag-doped TiO₂ on WO₃ nanoparticles (Ag@TiO₂/WO₃) was prepared by a modified sol-gel precipitation route, and their physicochemical properties were studied. The bandgap of Ag sensitized metal oxide nanocomposite in Ag@TiO₂/WO₃ was slightly reduced compared to the pristine titania due to the creation of interstitial energy states during colligation of titania and tungsten oxide. The ease of charge carrier transfers through the heterojunction of TiO₂/WO₃ increased the photocatalytic activity of the photocatalyst. Furthermore, in Ag@TiO₂/WO₃ the plasmonic Ag sensitization to the host semiconductor TiO₂ has further boosted the rate of photocatalytic degradation because of the surface plasmon resonance (SPR) and hindrance of charge carrier recombination. Due to the synergistic effect of SPR and the presence of heterojunction in Ag@TiO₂/WO₃, the photocatalytic activity was found to be 25 times higher for Ag@TiO₂/WO₃ than that of commercial DP25 photocatalyst under visible light towards methylene blue degradation.

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1. Introduction

At present water resource contamination with organic pollutants from industries is a major cause of concern. Untreated wastewater from industry contains a high concentration of organic pollutants that can cause irreversible detriment to the environment and human health (Zhao et al., 2020). Methylene blue (MB) and methyl orange (Lu et al., 2019) are widely used dyes in small to large-scale industries that generate huge organic pollutants. Compared to methyl orange, MB is extensively used in paper, printing, textile, and food industries and thus remains a major organic pollutant. Furthermore, MB dye is toxic, hazardous, and mutagenic pollutants. Therefore, photocatalytic degradation of MB can be very beneficial towards attaining an eco-friendly environment. In this regard, researchers are continuously trying to develop efficient semiconductor photocatalysts that limit the usage of sacrificial agents (H_2O_2) under visible light. Because sacrificial agent's application in removing organic pollutants is not cost-effective.

TiO_2 photocatalyst is extensively explored for the removal of organic pollutants since its discovery in 1972 (Guo et al., 2019; Medhi et al., 2020; Kim et al., 2020b; Chen et al., 2018). Due to its fascinating properties, such as high stability towards photo-corrosion, desirable band-edge alignment relative to the oxidation-reduction potential of water, and abundance in nature, titania is considered to be the most potential candidate for the solar energy conversion into useful form of chemical or electrical energy (Lu et al., 2012; Zhang et al., 2021). However, the unmodified pristine titania is not considered as a potent photocatalyst under visible light because of its relatively high bandgap (~ 3.2 eV) and fast charge carrier recombination rate. In order to address the major shortcomings of titania, several studies were carried out to enhanced visible light absorption and electron-hole separation through doping of cationic and anionic elements, making nanocomposites of different metal oxides and sensitization with the plasmonic metals (Tatsuma et al., 2002; Zhi et al., 2020; Serpone, 2006; Deguchi et al., 2001; Hao et al., 2017; Ding et al., 2019; Chen et al., 2008; Zhang et al., 2010; Olaniyan and Jeong, 2020; Kim et al., 2011).

Heterojunction of the host semiconductor with other low bandgap metal-oxides having different band edge positions is an excellent approach to amplify the carrier generation as well as separation under light illumination. Besides TiO_2 photocatalyst, low bandgap tungsten oxide (WO_3) is also regarded as a suitable candidate for hydrogen production, photocatalytic dye degradation, solar smart windows, and sensors (He et al., 2011; Ramkumar and Rajarajan, 2017; Xu et al., 2014). It is reported that $\text{CdS}/\text{TiO}_2/\text{WO}_3$ has high charge carrier transfer rate due to the potential gradient in the composites of ternary hybrid semiconductors (Kim et al., 2011). In such a ternary system, only the CdS is optically active in visible light ($\lambda > 495$ nm), and photogenerated electrons in the conduction band (CB) of CdS get detached from holes and migrates to relatively lower CB edges of TiO_2 and WO_3 in a cascaded way. Furthermore, nanohybrid photocatalyst of TiO_2 and WO_3 is reported as an excellent charge storage material (Zhao et al., 2009). The TiO_2/WO_3 composite band structure has a staggered gap (type II) where the CB minimum of WO_3 is lower than the CB minimum of TiO_2 . This kind of band structure enables the electron migration from CB of TiO_2 into the CB of WO_3 and the holes drift from WO_3 valence band (VB) to TiO_2 (Hao et al., 2017; Zhang et al., 2010; Anandan and Miyauchi, 2012).

Sensitization of plasmonic metals (such as Ag, Au and Pt) with the host metal-oxide semiconductors has gained considerable interest due to localized surface plasmon resonance (LSPR) absorption under visible light range (Awazu et al., 2008; Liu et al., 2011). Plasmonic hot electron generation and charge carrier transfer are the main mechanisms demonstrated for various applications, including photocatalytic decomposition, plasmonic solar cells, nanophotonic circuitry, and near-field infrared imaging (Luther et al., 2011). The creation of a surface plasmon resonance (SPR) induced localized electric field on the metal surface boosts the electron-hole pair generation in the host

photocatalyst and readily separates them, and thereby increases the efficiency of the photocatalyst. The surface plasmon resonance strength depends on the quality factor of the plasmonic materials. Among the plasmonic metals, Ag has a cost advantage and gaining interests due to its large quality factor across the spectrum of range 300–1200 nm (Rycenga et al., 2011). In Ag sensitized TiO_2 , the excited electrons on the metal surface is due to SPR, which migrates from the metal to the CB of TiO_2 , leaving a positive ion that was compensated by the donor ion from solution during photocatalytic reaction (Luther et al., 2011; Ramchiary et al., 2016).

In this study, silver nanoparticle (Ag) sensitized staggered gap heterojunction between TiO_2 and WO_3 was synthesized by following modified sol-gel precipitation route, and the photocatalytic performance was investigated under the visible light without using any sacrificial agent. $\text{Ag@TiO}_2/\text{WO}_3$ photocatalyst exhibited higher MB degradation compared with other reported catalysts.

2. Experimental section

2.1. Chemicals applied

Titanium isopropoxide $\{\text{Ti}(\text{OCH}(\text{CH}_3)_2, 97\% \text{ purity}\}$, and tungstic acid $\{\text{H}_2\text{WO}_4, 99\%\}$ were purchased from Alfa Aesar and Loba Chemie, respectively. Silver nitrate $\{\text{AgNO}_3, 99.8\%\}$, isopropanol $\{(\text{CH}_3)_2\text{CHOH}, 99\%\}$, and nitric acid $\{\text{HNO}_3, 69\%\}$ were purchased from Merck, India. The solvent (water) used during the experiment procedures was double distilled and deionized.

2.2. Synthesis of pristine and heterojunctions nanoparticles

Initially, to prepare pristine titania (TiO_2), a solution of titanium isopropoxide and isopropanol with a 1:15 v/v ratio was mixed and stirred vigorously. Next, 1 M concentrated HNO_3 was poured to the solution. Afterward, 0.5 ml deionized water was poured dropwise at uniform stirring condition. This mixture solution was left undisturbed 24 h for aging to obtain the gel form. Subsequently, the gel was heated at 80–100 °C and dried. The final product was then pulverized to get the powder form and calcined at 500 °C for an hour. Thus, TiO_2 nanoparticle was obtained and later used for photocatalytic degradation of MB. Next, tungsten oxide (WO_3) was synthesized in a similar process. Again, TiO_2/WO_3 heterojunction (1:1 M ratio) was prepared and evaluated using different characterization methods.

Initially, stoichiometric amount of tungstic acid (H_2WO_4) was dispersed in 2-propanol and mixed vigorously at ambient temperature for 2 h. Next, this solution was mixed with the titania solution prepared earlier. Subsequently, the mixed solution was left for aging to obtain the gel form and dried at 80 °C for 12 h. Finally, the obtained powder after pulverization was calcined at 500 °C for an hour. To synthesis silver sensitized TiO_2/WO_3 heterojunction, AgNO_3 solution (1 wt%) was added to the titania solution and then mixed with a liquid blend of tungstic acid under constant string condition. Next, the formation of the gel takes place after undergoing a similar process mentioned above, and subsequently, washed, dried, and calcined at 500 °C for an hour. This resultant final product is denoted as $\text{Ag@TiO}_2/\text{WO}_3$. The schematic diagram of synthesis $\text{Ag@TiO}_2/\text{WO}_3$ photocatalyst is shown in Fig. S1 in the supplementary information (SI).

2.3. Characterization of photocatalysts

To determine the structural properties and crystalline phases of the prepared materials, Bruker AXS D8 Advance X-ray diffractometer possessed with $\text{CuK}\alpha$ radiation (1.54 Å) was used. The morphological properties of the samples were examined by using transmission electron microscope (TEM, FEI-Tecna G2 F20S-Twin) operated at 200 kV. Ultraviolet-visible (UV-vis) diffuse reflectance spectroscopy (DRS) (Shimadzu UV-2200) was used for analyzing the absorption spectra of

the samples. Raman spectrophotometer (Renishaw) and photoluminescence (PL) spectrophotometer (PerkinElmer LS55) were used to study the structural change and defect states in the crystal. ESR signals were recorded using electron spin resonance (ESR) spectrometer (JEOL, JES-FA200) to investigate the paramagnetic species. The surface elements and electronic state of the as-prepared photocatalysts were investigated using X-ray photoelectron spectroscopy (XPS) (ESCA, Instrument, VSW, UK) equipped with a Al K α x-ray radiation source.

2.4. Photoactivity of catalysts for MB degradation

The photoactivity of the as-prepared catalysts was investigated under the visible light source (Radium, Relogen PAR30, China), of intensity 121 W m⁻². The photocatalytic activity was evaluated based on the degradation of MB dye with 0.01 M concentration and 0.5 g L⁻¹ photocatalyst loading. Photoactivity of commercial photocatalyst Degussa P25 (DP25) was also evaluated for reference. The adsorption-desorption equilibrium was studied by keeping the material-loaded suspension in the dark place for an hour. The solution was then illuminated by visible light and then the samples were collected consecutively at an interval of 15 min for test (Ramchiary et al., 2016).

3. Results and discussion

3.1. XRD, UV-Vis spectra, and photoluminescence spectra analysis

Fig. 1a depicts the XRD spectra of TiO₂, WO₃, TiO₂/WO₃, and Ag@TiO₂/WO₃. TiO₂ exhibited diffraction peaks at 2 θ = 25.1°, 37.8°, 48.1°, 53.8°, and 54.9° (PDF: 89-4921) that are assigned to the anatase phase of titania, representing the planes (101), (004), (200), (105), and (211), respectively. The XRD peaks of WO₃ at 2 θ = 23.1, 23.5°, 24.2°, 28.6°, 34.1°, 41.7°, 49.9°, 55.1°, 55.9°, and 62.2° (PDF: 83-0950) were corresponded to the plane (002), (020), (200), (112), (202), (222), (400), (402), (420), and (304), respectively, and are attributed to the monoclinic structure of tungsten oxide (Ham et al., 2010). The presence of TiO₂ and WO₃ in the as-prepared catalysts TiO₂/WO₃ and Ag@TiO₂/WO₃ was confirmed from the XRD spectra. The estimated crystallite size (using Scherrer's equation) of the pristine titania and tungsten oxide nanoparticles are ~17 and ~21 nm, respectively. The average crystallite size of TiO₂ and WO₃ in both the TiO₂/WO₃ and Ag@TiO₂/WO₃ photocatalyst was found to be ~11 and ~18 nm, respectively.

The absorbance spectra of pristine TiO₂, WO₃, TiO₂/WO₃, and Ag@TiO₂/WO₃ are shown in Fig. 1b. The absorption onset of pristine TiO₂ is found to be in the ultraviolet range with a sharp absorption edge at around 388 nm. On the other hand, the pristine WO₃ exhibited a broad absorption spectrum in the visible region. Further the absorption spectra related to the heterojunction TiO₂/WO₃ and Ag@TiO₂/WO₃ photocatalysts were also broad and noticed to be red-shifted as compared to the pristine titania. This red-shift is mainly due to the creation of mid-gap states in the bandgap of titania because of the lattice mismatch between the metal oxides. The absorption peak about 580 nm in the Ag@TiO₂/WO₃ catalyst was ascribed to the SPR effect exhibited by metallic Ag nanoparticles (Awazu et al., 2008). The SPR phenomena enhanced the visible light harvesting, and thus increases the photocatalytic efficiency of the catalyst (Ramchiary et al., 2016).

The photocatalytic activity was evaluated based on the degradation of MB dye with 0.01 M concentration and 0.5 g L⁻¹ photocatalyst loading. Photoactivity of commercial photocatalyst Degussa P25 (DP25) was also evaluated for reference. The adsorption-desorption equilibrium was studied by keeping the material-loaded suspension in the dark place for an hour. The solution was then illuminated by visible light and then the samples were collected consecutively at an interval of 15 min for test (Ramchiary et al., 2016).

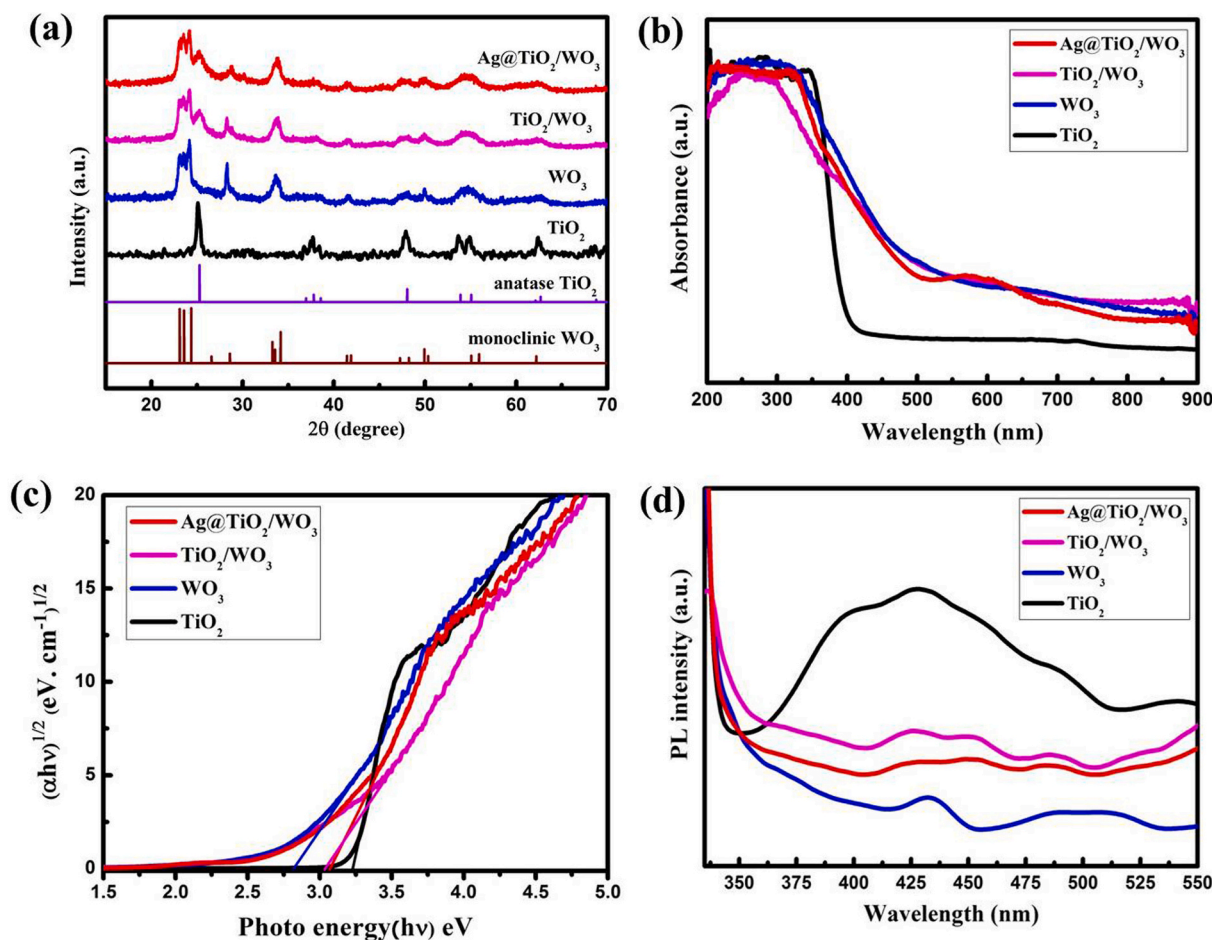


Fig. 1. (a) X-ray diffraction, (b) UV-Visible, and (d) photoluminescence spectra (at the excitation wavelength 330 nm) of TiO₂, WO₃, TiO₂/WO₃, and Ag@TiO₂/WO₃. (c) Bandgap calculation of TiO₂, WO₃, TiO₂/WO₃, and Ag@TiO₂/WO₃ using Tauc's method.

Bandgap of the prepared photocatalyst was calculated implicating Tauc's formula given by:

$$(\alpha \cdot h\nu)^{1/n} = A (h\nu - E_g) \quad (1)$$

where A , α , E_g , and $h\nu$ are the constant, absorption coefficient, energy gap and photon energy, respectively. The value of n depends on the nature of transition process (Ramchiary et al., 2016). The bandgap is estimated by plotting $(h\nu)$ vs. $(\alpha \cdot h\nu)^{1/2}$, as shown in Fig. 1c. The estimated bandgap values for pristine TiO_2 and WO_3 were ~ 3.23 eV and ~ 2.82 eV, respectively (Kalanur, 2019). On the other hand, the bandgap of TiO_2/WO_3 and $\text{Ag@TiO}_2/\text{WO}_3$ was ~ 3.04 eV and ~ 3.07 eV, respectively. Upon Ag sensitization in TiO_2/WO_3 heterojunction, further reduction in the bandgap for $\text{Ag@TiO}_2/\text{WO}_3$ was not detected, which apparently indicated that the sensitization of Ag nanoparticles mainly on the surface of TiO_2 .

Photoluminescence (PL) spectra of the photocatalysts at room temperature was investigated to identify the defect states that is accountable for visible light absorption. Fig. 1d illustrates the PL spectra of pristine TiO_2 , WO_3 , TiO_2/WO_3 , and $\text{Ag@TiO}_2/\text{WO}_3$. The PL emission at 392 nm and 428 nm of the pristine titania is attributed to onset band transition equivalent to the bandgap ~ 3.2 eV and photon assisted indirect transitions, respectively (Jovic et al., 2013; Serpone et al., 1995). The peak emission at 460 nm and 490 nm corresponds to the self-trapped excitons (STE) appearing due to the transition from lower levels in Ti^{3+} 3d states of TiO_2 to the deep acceptor levels created by OH^- (Chetibi et al., 2017; Mathew et al., 2012; Tang et al., 1993). The prominent transition peak of WO_3 at 433 nm is equivalent to the energy gap of tungsten oxide and is about ~ 2.8 eV. The peaks observed at around 421 nm and 450 nm are the primary band transitions of TiO_2/WO_3 and $\text{Ag@TiO}_2/\text{WO}_3$, respectively, corresponding to energy gap ~ 3.0 eV and ~ 2.7 eV. The transition due to STE is observed at 488 nm in both the sample. In addition, the emission spectra at 525 nm in TiO_2/WO_3 and $\text{Ag@TiO}_2/\text{WO}_3$ is attributed to the surface shallow trap (oxygen vacancy) transitions (Jovic et al., 2013). Such transition peak due to surface shallow traps is not observed in both the pristine TiO_2 and WO_3 . The quenching of the PL peak observed in TiO_2/WO_3 compared to the pristine TiO_2 is ascribed to the carrier's separation due to the potential gradient in the TiO_2/WO_3 heterojunction. The charge separation was further increased in $\text{Ag@TiO}_2/\text{WO}_3$ as the electrons in the CB of semiconductors are extracted by Ag nanoparticles.

3.2. Raman spectra and ESR analysis

Raman spectra of the photocatalysts are shown in Fig. 2a. For pristine titania, six Raman vibrational modes are detected at around 142 (E_g), 192 (E_g), 393 (B_{1g}), 511 (A_{1g}), 519 (B_{1g}) (superimposed with 511), 635 (E_g) cm^{-1} that corresponds to the anatase phase of titania. The Raman active modes at 272, 327, 712, and 804 cm^{-1} are attributed to the pure WO_3 . The allowed modes at 712 and 804 cm^{-1} are assigned to the O-W-O stretching type vibrations, and the peaks located at 272 and 327 cm^{-1} are induced by W-O-W bending type vibrations (Xu et al., 2014; Zamharir et al., 2014). The vibrational modes of both TiO_2 and WO_3 samples are observed in the composite system (shown in Fig. 2a). Comparing to pure TiO_2 , the Raman signals of TiO_2/WO_3 and $\text{Ag@TiO}_2/\text{WO}_3$ are slightly shifted to higher frequencies, which indicates the structural changes in TiO_2 due to the incorporation of WO_3 . The shifted peaks are now centered at 155, 256, 405, 526 (superimposed with A_{1g}) and 649 cm^{-1} . No significant shift was observed in the Raman signal of WO_3 , which implies that there is no structural distortion occurred in WO_3 .

The formation of oxygen vacancies or paramagnetic species has been investigated through ESR study. Fig. 2b illustrates the ESR spectra recorded at room temperature for the as-prepared photocatalysts. Pristine TiO_2 and WO_3 , are not shown any prominent ESR signal, indicating the stoichiometric composition and absence of oxygen vacancies in the

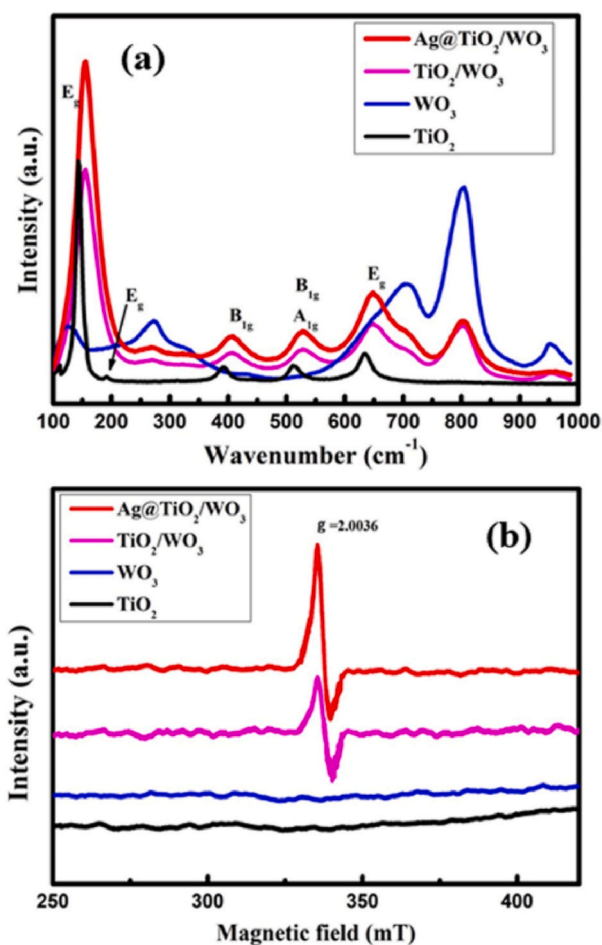


Fig. 2. (a) Raman spectra and (b) Electron spin resonance (ESR) spectra of TiO_2 , WO_3 , TiO_2/WO_3 , and $\text{Ag@TiO}_2/\text{WO}_3$.

pure form (Yoon et al., 2011). In the TiO_2/WO_3 sample, a significant resonance peak was detected at g -factor = 2.0036. This suggested the presence of surface h^+ trapping species (Yang et al., 2010; Dimitrijevic et al., 2007). The creation of trapping center or species was possibly due to the vacancy formation near the interface owing to the lattice mismatch between the two metal-oxides (Kim et al., 2020a, 2020b, 2020c). The $\text{Ag@TiO}_2/\text{WO}_3$ heterojunction demonstrated slightly enhanced ESR intensity, implying more creation of oxygen vacancies due to the transfer of electrons to the Ag metal (Pu et al., 2018).

3.3. XPS analysis of photocatalysts

The electronic states and presence of surface elements of the photocatalysts were investigated using XPS. Fig. 3a shows the individual full survey spectrum of pristine TiO_2 , TiO_2/WO_3 , and $\text{Ag@TiO}_2/\text{WO}_3$ that revealed the co-existence of the major elements C, Ti, O, Ag, and W. The observed C signal at 285.6 eV is assigned to the extraneous carbon-based contaminants (Ramchiary et al., 2016). The high-resolution XPS profile of $\text{Ti}(2p)$, $\text{O}(1s)$, $\text{W}(4f)$, and $\text{Ag}(3d)$ are illustrated in Fig. 3b, c, d, and e, respectively. The $\text{Ti}(2p)$ spectra at the binding energy 466.0 and 460.3 eV in Fig. 3b, is related to $\text{Ti}(2p_{1/2})$ and $\text{Ti}(2p_{3/2})$ state, respectively, which corresponds to the Ti^{4+} oxidation state of TiO_2 (Zamharir et al., 2014; Ramchiary et al., 2016). In TiO_2/WO_3 sample, a slight shift of the $\text{Ti}(2p)$ line is observed (about 0.7 eV) towards the lower binding energy. This shift indicates the ease of carrier transfer through the junction between TiO_2 and WO_3 (Verma et al., 2015).

The spectrum obtained for $\text{O}(1s)$ peak at around 530.9 eV for pristine TiO_2 (shown in Fig. 3c) is assigned to the surface bridging oxygens

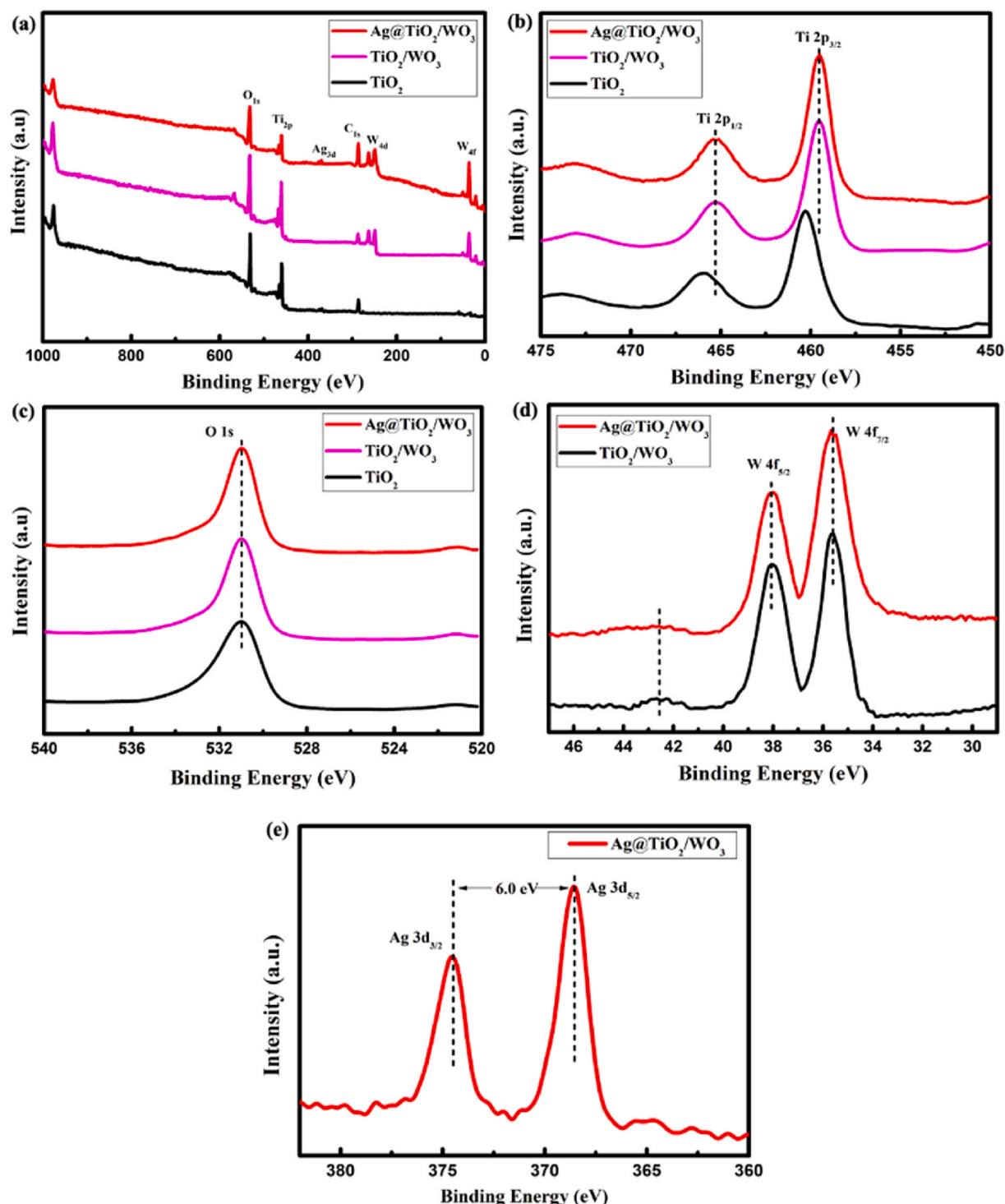


Fig. 3. XPS spectra of TiO_2 , TiO_2/WO_3 , and $\text{Ag@TiO}_2/\text{WO}_3$. (a) Survey scan. High-resolution spectra of (b) $\text{Ti } 2p$, (c) $\text{O } 1s$, (d) $\text{W } 4f$, and (e) $\text{Ag } 3d$, respectively.

(Ti-O) (Stojadinovic et al., 2012). The two main XPS resolved peaks of TiO_2/WO_3 and $\text{Ag@TiO}_2/\text{WO}_3$ at binding energy 38.0 eV and 35.6 eV shown in Fig. 3d, are ascribed to the doublets of WO_3 , ($\text{W } (4f_{5/2})$ and $\text{W } (4f_{7/2})$ state), which is attributed to the W^{6+} -oxidation state of the material (Stojadinovic et al., 2012). The spin-orbit splitting and peak ratio of the doublet was found to be 2.4 eV and ~ 0.75 , respectively. The broad peak located at 42.5 eV is attributed to $\text{W } (5p_{3/2})$ state. Fig. 3e shows the high-resolution $\text{Ag } (3d)$ spectrum consist of spin-orbit components at 368.5 eV and 374.5 eV, ascribing the $\text{Ag } (3d_{5/2})$ and $\text{Ag } (3d_{3/2})$ states, respectively (Ramchiary et al., 2016). The energy difference between

the two spin-orbit components is 6.0 eV, which reveals the presence of metallic silver nanoparticles (Ag^0) (Ramchiary et al., 2016; Zhang et al., 2012).

3.4. TEM analysis of synthesized photocatalyst

To study the surface morphologies of the photocatalysts, SEM analysis was performed. Fig. S2 illustrates the SEM image of (a) pristine TiO_2 , and (b) $\text{Ag@TiO}_2/\text{WO}_3$. The aggregation of the particles of the range 50–100 nm are observed in both the sample with uniform

distributions. However, a substantial change in the morphology of the Ag@TiO₂/WO₃ sample is seen with more clustered distribution. To explore further about the morphologies and particle size of the prepared samples, TEM and HR-TEM were studied. Fig. 4 shows the TEM and HR-TEM image of pristine TiO₂ (a–b), pristine WO₃ (c–d), TiO₂/WO₃ (e–f), and Ag@TiO₂/WO₃ (g–i), at different magnifications. The interplanar spacing (*d*) of pristine TiO₂ and WO₃ (shown the magnified view in Fig. 4b and d, respectively) are found to be ~ 0.34 and ~ 0.38 nm, respectively, equivalent to the *d* values of titania (anatase phase) and tungsten oxide (Xu et al., 2014; Yoon et al., 2011).

Further the average particle size of TiO₂ was ~ 20 nm, which is in agreement with the XRD analysis. From Fig. 4f, two distinct interplanar spacing (*d*), corresponding to TiO₂ (3.2 Å) and WO₃ (3.8 Å), are observed in the TiO₂/WO₃ matrix. The particle sizes of Ag nanoparticles were 10–15 nm (presented in Fig. 4h). The *d* spacing of Ag nanoparticle was 2.3 Å and corresponded to (111) plane as shown in the inset of Fig. 4i (Ramchiary et al., 2016).

3.5. Photocatalytic activity test

Fig. 5a shows the photocatalytic degradation of methylene blue (MB) with and without light illumination ($\lambda \geq 400$ nm), in absence of any sacrificial chemical agent. In this experiment, photocatalytic activity of Degussa P25 was examined for reference. The degradation of MB by the catalysts via adsorption (–60 to 0 min) was found to be insignificant. Fig. 5a (0–60 min) illustrates the degradation profile of MB with the prepared photocatalysts under visible light of wavelength $\lambda \geq 400$ nm. The resultant degradation percentage was found to be 72, 40, 19, 7, and 6 % for Ag@TiO₂/WO₃, TiO₂/WO₃, WO₃, TiO₂, and DP25, respectively, in comparison with their initial concentration. The degradation of control and material loaded MB concentration under visible light was monitored at maximum absorption wavelength 664 nm (shown in SI, Fig. S3 a–d). The rate constant of the degradation of MB was determined by plotting $\ln C/C_0$ vs. time graph as shown in Fig. 5b. In addition, an optical image of the MB degradation by TiO₂, TiO₂/WO₃, and Ag@TiO₂/WO₃ is presented in Fig. 5c–e. It is evident that Ag@TiO₂/WO₃ exhibited higher degradation of MB compared to other photocatalysts.

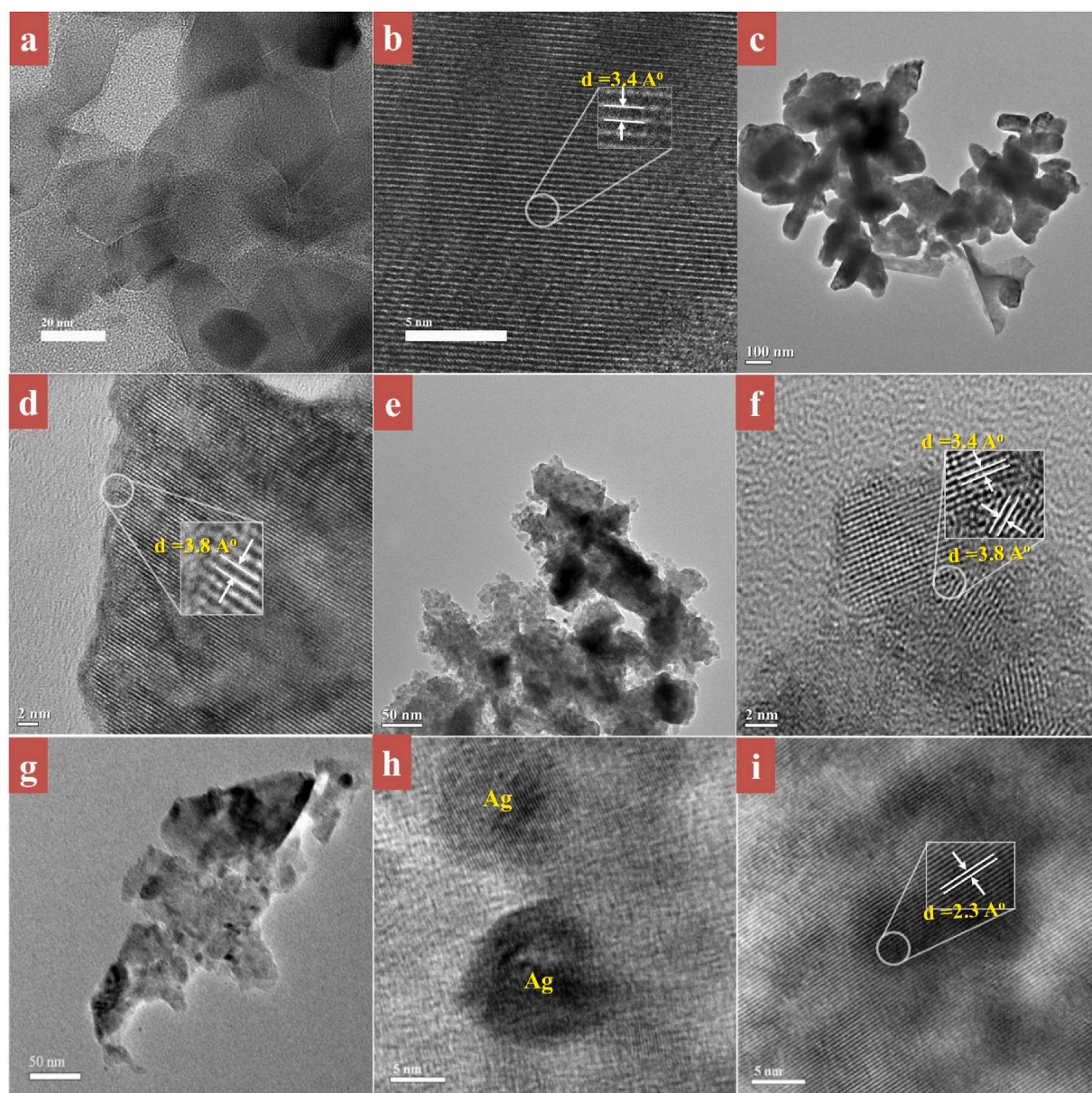


Fig. 4. TEM and HR-TEM images depiction of pristine (a–b) TiO₂, (c–d) WO₃, (e–f) TiO₂/WO₃, and (g–i) Ag@TiO₂/WO₃ at different magnifications.

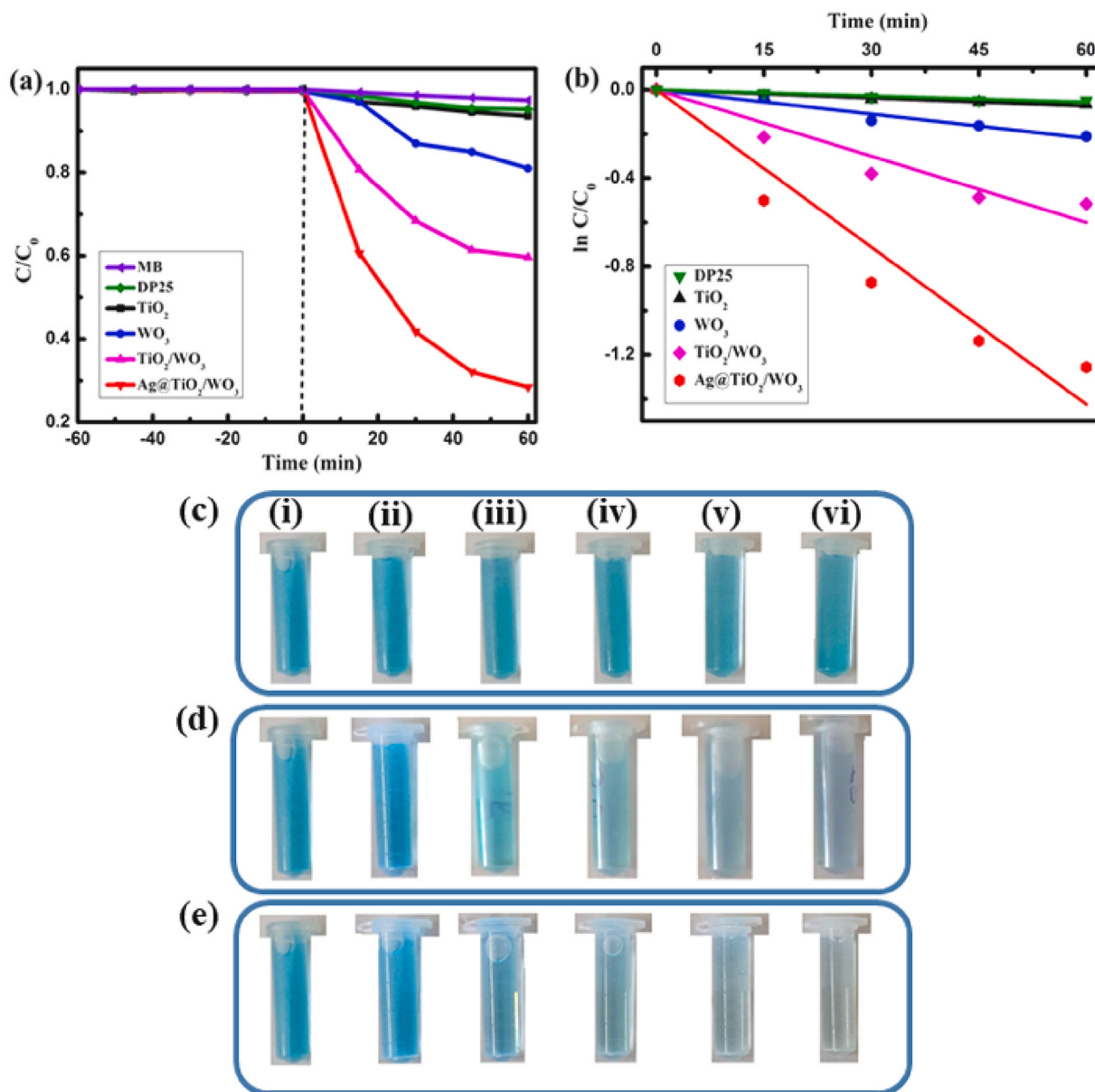


Fig. 5. (a) Photocatalytic degradation of MB without (60–0 min) and with visible light (0–60 min) using TiO_2 , WO_3 , TiO_2/WO_3 , and $Ag@TiO_2/WO_3$ photocatalyst. (b) Plot of $\ln C/C_0$ vs Time. Optical image of (c) TiO_2 , (d) TiO_2/WO_3 , and (e) $Ag@TiO_2/WO_3$. (i) Pristine MB, (ii) 5, (iii) 15, (iv) 30, (v) 45, and (vi) 60 min.

The degradation of the controlled MB, and TiO_2 and WO_3 loaded MB are found to be insignificant under the visible light illumination. However, a small increase in the degradation was observed with the sample TiO_2/WO_3 . Notably, the degradation of MB with the sample $Ag@TiO_2/WO_3$ was found significantly enhanced. The rate of degradation (k) are found to be $9.2 \times 10^{-4} \text{ min}^{-1}$, $1.2 \times 10^{-3} \text{ min}^{-1}$, $3.6 \times 10^{-3} \text{ min}^{-1}$, $10.01 \times 10^{-3} \text{ min}^{-1}$, and $23.5 \times 10^{-3} \text{ min}^{-1}$ for DP25, TiO_2 , TiO_2/WO_3 , and $Ag@TiO_2/WO_3$, respectively. Prior studies related to the photocatalytic degradation of MB dye using TiO_2/WO_3 based heterojunction are summarized in Table 1.

The rate of degradation using $Ag@TiO_2/WO_3$ was enhanced up to ~20 and ~25 times than that of pristine TiO_2 and Degussa P25, respectively. This augmentation in the activity was related to the synergy of (i) localized electric field due to SPR of Ag nanoparticles and (ii) swift detachment of photogenerated electron-hole pairs through the interface of TiO_2/WO_3 heterojunction. Since the electron affinity of WO_3 is more than TiO_2 , the photogenerated electrons readily undergoes migration from the CB of TiO_2 to WO_3 (Chen et al., 2016). However, the electrons present in the CB of WO_3 is incapable to degrade organic

pollutants due to the lower band alignment relative to the reduction potential of O_2/H_2O (Paula et al., 2019; Herron et al., 2015).

Fig. 6 depicts the schematic representation of photocatalytic degradation mechanism of $Ag@TiO_2/WO_3$ under visible light. Notably, VB position of WO_3 is lower than the VB position of TiO_2 , hence the photogenerated holes in the VB of WO_3 under light illumination preferably migrate towards the VB of TiO_2 (Meng et al., 2018). This transfer of charge carriers in TiO_2/WO_3 nanocomposites results in the reduction of photogenerated charge carrier recombination.

Moreover, a large number of free electrons are injected from excited plasmonic Ag nanoparticles into the CB of TiO_2 , leaving a positive charge (h^+) behind due to SPR induced localized field. Thus, it enhances the visible light absorption as well as increases the charge carrier concentration in the host TiO_2 photocatalyst and consequently, amplifies the photocatalytic reactions (Jing et al., 2013). The electrons present in the CB of TiO_2 react with surface O_2 and produce superoxide anion radicals ($\bullet O_2^-$) which yield H_2O_2 and subsequently, H_2O_2 produces photodegradation active species $\bullet OH$ radicals (Leong et al., 2014). Similarly, the holes in the VB of TiO_2 participates in the oxidation

Table 1Photocatalytic degradation of MB dye using TiO₂/WO₃ based heterojunction photocatalyst.

Photocatalyst	Synthesis method	Light source	Rate constant (min ⁻¹)	Reference
TiO ₂ /WO ₃	Electron beam evaporation	UV	6.92 × 10 ⁻³	Smith and Zhao, 2008
WO ₃ -MWCNT-TiO ₂	Sol-gel	UV	4.99 × 10 ⁻³	Lei et al. (2011)
V-WO ₃ /TiO ₂	Micro-arc oxidation process	LED 420–520 nm	6.0 × 10 ⁻³	Yeh et al. (2014)
WO ₃ /TiO ₂ microsphere	Spray drying method	Visible	1.97 × 10 ⁻³	Yang et al. (2014)
		UV	12.85 × 10 ⁻³	
nWO ₃ -TiO ₂	Facile one-pot precipitation	UV	42.4 × 10 ⁻²	Younas et al., 2019
WO ₃ /TiO ₂	Sol-gel	UV	18.5 × 10 ⁻³	Wahyuono et al. (2019)
Mesoporous WO ₃ /TiO ₂	Sol-gel	UV	17 × 10 ⁻³	El-Yazeed and Ahmed, 2019
Au-WO ₃ /TiO ₂	Hydrothermal method	Solar radiation AM1.5G	29.5 × 10 ⁻³	Yang et al. (2020)
C-TiO ₂ /WO ₃	Hydrothermal method	Visible (λ ≥ 400 nm)	3.5 × 10 ⁻³	Kim et al. (2020a, 2020b, 2020c)
WO ₃ /TiO ₂ sphere	Sol-gel	Visible	6.5 × 10 ⁻³	Zhao et al. (2021)
Ag@TiO ₂ /WO ₃	Sol-gel	Visible	23.5 × 10 ⁻³	This study

counterparts. The rate of degradation of MB using Ag@TiO₂/WO₃ was ~20 and ~25 times higher in contrast with pristine TiO₂ and Degussa P25, respectively. This increase in the photocatalytic performance of Ag@TiO₂/WO₃ heterojunction was because of the synergistic effect (i) enhancement of light-harvesting and a large number of charge carrier injection due to SPR effect exhibited by Ag nanoparticles under the illumination of visible light, and (ii) lower recombination rate due to ease of charge carrier transfer through the junction between the two metal oxides. Thus, Ag@TiO₂/WO₃ photocatalyst can be a promising candidate towards MB degradation in absence of any sacrificial agent like H₂O₂ under visible light.

Authorship contributions

Conception, design, and experimentation: B. Basumatary, R. Basumatary, A. Ramchiary. Drafting the Manuscript and data interpretation: B. Basumatary, R. Basumatary, A. Ramchiary, and D. Konwar.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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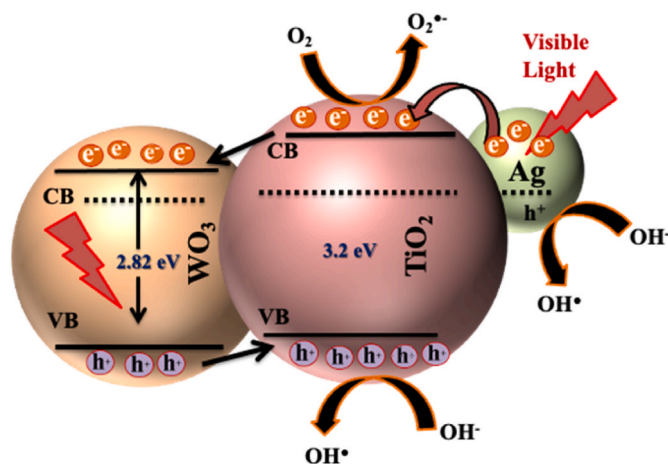
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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2021.131848>.

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**Fig. 6.** Schematic illustration of Ag@TiO₂/WO₃ heterojunction photocatalyst.

reaction of adsorbed water molecules to produce hydroxyl radicals (OH•). Additionally, the positively charged photogenerated holes on Ag nanoparticles may potentially degrade the adsorbed pollutant directly (Jing et al., 2013; Li et al., 2018). The photocatalytic dye degradation reactions are discussed in SI.

4. Conclusion

In summary, the plasmonic Ag nanoparticle sensitized heterojunction of TiO₂/WO₃ (Ag@TiO₂/WO₃) was successfully synthesized using the modified sol-gel route. The photocatalytic activity of Ag@TiO₂/WO₃ was significantly enhanced compared to its

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