

Research Paper

Synergistic $\text{PW}_{12}\text{O}_{40}^{3-}$ oxidation and TiAl-SBA-15 photocatalysis in $\text{PW}_{12}\text{O}_{40}^{3-}/\text{NH}_3^+$ -TiAl-SBA-15 for highly efficient dibenzothiophene desulfurization

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ABSTRACT

In this study, a novel composite catalyst, $\text{PW}_{12}\text{O}_{40}^{3-}/\text{NH}_3^+$ -TiAl-SBA-15 (denoted as $\text{PW}@\text{TiAl-SBA-15}$), was successfully synthesized by immobilizing phosphotungstic acid (HPW) through 3-aminopropyltriethoxysilane (APTES) and integrating it with a TiAl-SBA-15 photocatalyst for the oxidative desulfurization of dibenzothiophene in diesel fuel. The incorporation of HPW introduces a reversible $\text{W}^{6+}/\text{W}^{5+}$ redox cycle, which significantly promotes the efficient utilization and activation of hydrogen peroxide. The synergistic interaction among the multiple catalytic components enhances H_2O_2 activation, facilitating the formation of reactive peroxotungstate species and oxygen-derived radicals ($\cdot\text{OOH}/\cdot\text{O}_2$). These effects were systematically confirmed by H_2 -TPR, XPS, UV-Vis diffuse reflectance spectroscopy, and radical scavenging experiments. As a result, the $\text{PW}@\text{TiAl-SBA-15}$ catalyst exhibits outstanding photocatalytic oxidative desulfurization performance under mild conditions (50 °C), achieving nearly complete DBT removal within 100 min under visible-light irradiation. Furthermore, the catalyst demonstrates excellent stability and reusability, maintaining over 98.83% desulfurization efficiency after five successive regeneration cycles. The photocatalytic oxidation process over the $\text{PW}@\text{TiAl-SBA-15}$ catalyst follows pseudo-first-order kinetics, with an apparent activation energy of 28.143 kJ·mol⁻¹. This work provides valuable insights into the rational design of efficient, stable, and environmentally benign photocatalysts for sulfur removal from fuels, contributing to global efforts toward cleaner and more sustainable energy systems.

1. Introduction

Sulfur-containing compounds in petroleum-derived fuels are major contributors to atmospheric pollution and acid rain formation, necessitating increasingly stringent fuel desulfurization regulations. Although catalytic hydrodesulfurization (HDS) remains the dominant industrial technology, its limited efficiency toward refractory aromatic sulfur compounds and harsh operating conditions have motivated the development of alternative approaches. Among them, oxidative desulfurization (ODS) has emerged as an attractive strategy because sulfur compounds can be selectively oxidized into highly polar sulfones under relatively mild conditions, facilitating their subsequent removal from fuel matrices [1–3]. Among refractory sulfur compounds, dibenzothiophene (DBT) remains one of the most challenging molecules because of its aromatic stability and low reactivity toward conventional HDS

processes. Therefore, developing efficient catalyst systems capable of promoting DBT oxidation under mild conditions remains an important objective for practical ODS applications.

Among various oxidation catalysts investigated for ODS, transition-metal-based systems have attracted considerable attention due to their tunable redox properties and oxidant activation capability. In particular, tungsten-containing materials, especially polyoxometalates (POMs), exhibit remarkable catalytic performance owing to their strong acidity and reversible redox behavior [4–9]. Phosphotungstic acid (HPW, $\text{H}_3\text{PW}_{12}\text{O}_{40}$), containing Keggin-type $\text{PW}_{12}\text{O}_{40}^{3-}$ anions, is regarded as one of the most effective oxidation catalysts because the reversible transformation between W^{6+} and W^{5+} species facilitates H_2O_2 activation and oxygen transfer during sulfur oxidation reactions.

Immobilization of PW species onto heterogeneous matrices has been widely explored to improve catalyst stability and recovery.

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Representative examples include ionic-liquid-supported systems, carbon quantum dot composites [10], heterogeneous $\text{CuWO}_4/\text{SiO}_2$ catalysts [11], quaternary ammonium phosphotungstate photocatalysts [12], Ce-doped HPW/ TiO_2 composites [13], HPW/ TiO_2 nanocomposites [14], and multifunctional $\text{Ti}/\text{TiO}_2/\text{NiWO}_4 + \text{WO}_3$ systems [15]. Despite their high oxidation activity, most PW-based systems still rely predominantly on thermal activation and insufficiently utilize sustainable energy sources for oxidant activation.

Integrating photocatalytic pathways with oxidation catalysts offers an attractive strategy for improving oxidant activation and energy efficiency during ODS. Semiconductor photocatalysts can utilize light energy to generate charge carriers and reactive oxygen species that accelerate oxidation reactions. In mesoporous silica systems, Ti incorporation can generate additional active sites while maintaining excellent structural stability [16,17], although strong acidic synthesis conditions may hinder framework incorporation through Ti-O-Si hydrolysis, motivating approaches such as pH-controlled synthesis and fluoride-assisted regulation [18,19].

Various mesoporous and semiconductor-based photocatalysts, including MoO_3/SBA systems [20], Ag-AgBr/Al-MCM-41 [21], $\text{TiO}_2/\text{SBA-16}$ [22], $\text{CeO}_2\text{-V}_2\text{O}_5$ [23], and g-C₃N₄-supported MoO_3 [24], have demonstrated promising sulfur oxidation performance through enhanced light harvesting and oxidant activation. In addition, Ti-containing mesoporous supports such as NiMo/Ti-SBA-15 have also shown potential for sulfur removal applications [25]. Nevertheless, efficient coupling between photocatalytic charge transfer and oxidation-active redox centers remains a major challenge.

Among mesoporous photocatalytic supports, TiAl-SBA-15 is particularly attractive because its highly ordered pore structure provides favorable diffusion pathways for relatively large DBT molecules while maintaining high surface area and structural stability [26–28]. Simultaneous incorporation of Ti and Al species introduces multifunctional catalytic features, where Ti species may contribute to light absorption and charge transfer processes associated with reactive oxygen species generation, while Al species enhance surface acidity and adsorption properties. Consequently, TiAl-SBA-15 represents a promising platform for immobilizing redox-active oxidation species and constructing multifunctional ODS catalysts.

Despite extensive studies on PW-based oxidation catalysts and Ti-containing photocatalytic materials, constructing integrated systems capable of coupling photocatalytic charge separation with PW-mediated redox oxidation for efficient visible-light-assisted DBT oxidation remains insufficiently explored. Therefore, in this work, TiAl-SBA-15 was synthesized and functionalized with aminopropyl groups to enable electrostatic immobilization of $\text{PW}_{12}\text{O}_{40}^{3-}$ species, yielding the $\text{PW}_{12}\text{O}_{40}^{3-}/\text{NH}_3^+\text{-TiAl-SBA-15}$ catalyst. The resulting material was comprehensively characterized and systematically evaluated for DBT oxidative desulfurization using H_2O_2 under visible-light irradiation. This study aims to elucidate the synergistic interaction between $\text{PW}_{12}\text{O}_{40}^{3-}$ oxidation pathways and TiAl-SBA-15 photocatalytic activity toward the rational design of highly efficient visible-light-assisted DBT oxidation catalysts.

2. Experimental

2.1. Surface functionalization of TiAl-SBA-15

Surface functionalization was carried out by dispersing TiAl-SBA-15 in ethanol at a ratio of 0.5 g per 20 mL and refluxing under continuous stirring. APTES was then added at a ratio of 0.5 g TiAl-SBA-15 to 0.5 mL APTES, and the mixture was maintained at 80 °C for 24 h. The resulting solid was filtered and dried to yield amino-functionalized $\text{H}_2\text{N-TiAl-SBA-15}$.

TiSBA-15 was prepared by reported method [11]. The detail synthesis of this material are given in Supporting Information.

2.2. Synthesis of $\text{PW}_{12}\text{O}_{40}^{3-}/\text{NH}_3^+\text{-TiAl-SBA-15}$

The $\text{PW}_{12}\text{O}_{40}^{3-}/\text{NH}_3^+\text{-TiAl-SBA-15}$ catalyst was synthesized to enhance the immobilization of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ on the surface of $\text{H}_2\text{N-TiAl-SBA-15}$. This was achieved by protonating the surface amine groups using triflic acid, thereby generating positively charged $-\text{NH}_3^+$ species that promote strong electrostatic interactions with $\text{PW}_{12}\text{O}_{40}^{3-}$ anions. Briefly, 0.5 g of $\text{H}_2\text{N-TiAl-SBA-15}$ was dispersed in 25 mL of acetonitrile, followed by the addition of 2.0 mL of triflic acid solution. The mixture was refluxed at 80 °C for 5 h, then filtered and washed with acetonitrile to remove unreacted acid, yielding protonated $^+\text{H}_3\text{N-TiAl-SBA-15}$. Subsequently, the obtained solid was introduced into 50 mL of methanol containing a predetermined amount of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ corresponding to 20, 30, 40, or 50 wt%. The suspension was refluxed at 65 °C for 5 h, filtered, and dried under vacuum at 80 °C overnight. The final catalysts were denoted as x% PW@TiAl-SBA-15 (x = 20, 30, 40, and 50).

2.3. Photocatalytic oxidative desulfurization of dibenzothiophene

In the photocatalytic oxidative desulfurization experiments, direct sunlight was employed as the energy source (summer sunlight between 13:00 and 15:00), with a solar irradiance of approximately 900 W/m², corresponding to an illuminance of ~108,000 lx. The photocatalytic activity of the PW@TiAl-SBA-15 nanocomposite complex synthesized on DBT decomposition was studied with *n*-octane as a fuel sample. In the tests, 50 mL of DBT (300 ppm) and 50 mg of the catalyst were added to a Pyrex three-neck flask and stirred magnetically. The experiments were conducted under varying conditions of time and temperature to assess the impact on the desulfurization process. Different concentrations of $\text{PW}_{12}\text{O}_{40}^{3-}$ catalyst (20, 30, 40 and 50% by weight) were tested to determine the optimal amount for effective DBT decomposition. The decrease in DBT concentration was monitored using a UV-Vis spectrophotometer, measuring the absorption at $\lambda_{\text{max}}=325$ nm. This measurement was utilized to determine the rate and efficiency of DBT attenuation. For each experiment, the equilibrium concentration of DBT was recorded as the initial concentration (C_0) to evaluate the progress of photocatalytic decomposition, which was determined according to Eq. S1. The DBT in the model fuel, as well as the sulfur-containing species generated during the desulfurization process, was quantitatively analyzed using gas chromatography-mass spectrometry.

3. Results and discussion

3.1. Structural characteristics

The phase composition of TiAl-SBA-15 and PW@TiAl-SBA-15 samples was analyzed using XRD, and the results are presented in Fig. 1A.

The small - angle XRD pattern, illustrated in Fig. 1A, reveals distinct and sharp diffraction peaks for the synthesized samples. The high-intensity peak at a 2θ value of 0.85° and two weaker peaks at 2θ values of 1.6° and 1.8° correspond to the (110) and (200) planes, respectively. These peaks indicate the symmetrical p6mm hexagonal 2D structure characteristic of the mesoporous Al-SBA-15 material [29]. Additionally, the peak intensity decreases with increasing PW content from 20% to 50%, likely due to partial obscuration of the porous structure in TiAl-SBA-15.

In the wide-angle XRD pattern [Fig. S1], the samples exhibit an amorphous structure typical of Al-SBA-15 samples. Notably, the PW@TiAl-SBA-15 sample does not display any distinct crystalline peaks for titanium or HPW phases. The absence of titanium peaks can be attributed to the integration of titanium precursors into the sol-gel process, substituting silicon isotopes within the Al-SBA-15 structure. Furthermore, the non-appearance of HPW peaks suggests effective immobilization of HPW within the mesoporous structure. This immobilization is likely facilitated by the binding of HPW to the TiAl-SBA-15 frameworks via amine groups, anchoring HPW in the pores and on the

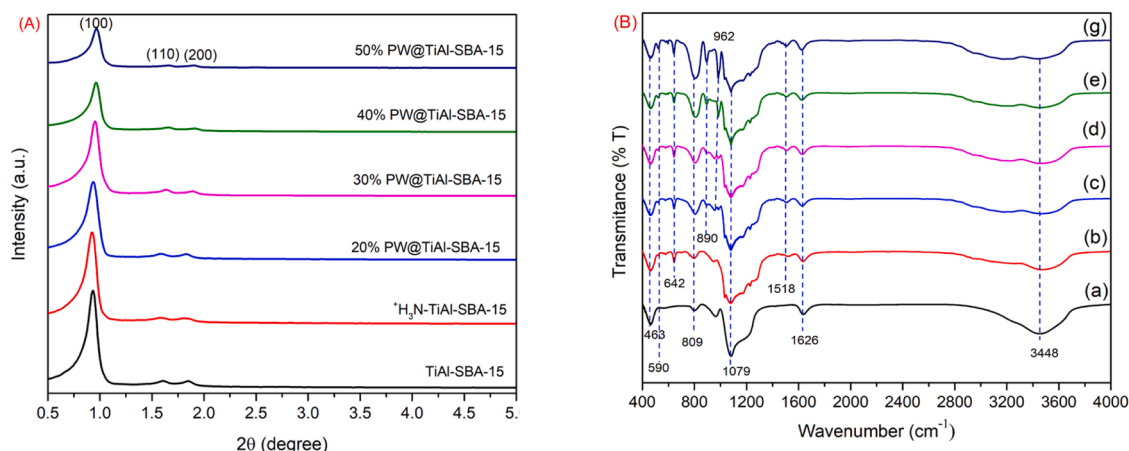


Fig. 1. (A) Small-angle of XRD pattern, and (B) FT-IR spectra of TiAl-SBA-15 and 20–50% PW@TiAl-SBA-15 samples.

surface of TiAl-SBA-15 [30]. Moreover, the absence of PW characteristic peaks suggests that PW is uniformly dispersed within the hexagonal channels of TiAl-SBA-15 due to chemical interaction between the PW active phase and TiAl-SBA-15 carrier.

The FT-IR spectroscopy analysis results for TiAl-SBA-15 and PW@TiAl-SBA-15 samples are presented in Fig. 1B. The FT-IR spectra reveal several characteristic vibrations indicative of the structural components within these samples. The FT-IR infrared spectra of both TiAl-SBA-15 and PW@TiAl-SBA-15 samples exhibit notable fluctuations. A prominent peak at 1079 cm⁻¹ is observed, which is associated with the asymmetric and symmetric vibrations of the Si-O-Si or Si-OH bonds. This peak is indicative of the stretching vibrations of the silanol group within the Al-SBA-15 structure [31]. Additionally, vibrations at a wavenumber of 590 cm⁻¹ are characteristic of the Ti-O-O vibrations [32]. The peak appearing at 3448 cm⁻¹ is identified as the stretching vibration of N-H bonds and silanol groups (Si-OH). The presence of bands around 3448 cm⁻¹, 1518 cm⁻¹, and 642 cm⁻¹ confirms the successful functionalization and formation of amine groups on the surface of the TiAl-SBA-15 material [33].

In the region of 1100 to 700 cm⁻¹, characteristic fluctuations are observed, which are attributed to the HPW acid group in the PW@TiAl-SBA-15 samples. Specifically, the oscillation at 1079 cm⁻¹ corresponds to the symmetric vibrational modes of the oxygen atoms bonded to phosphorus in the central PO₄³⁻ unit. The peak at 962 cm⁻¹ is assigned to the stretching vibration of the W=O bond, and the peak at 890 cm⁻¹ is associated with the asymmetric W-O-W vibrations in the anionic PW⁻ structure [34]. These characteristic peaks are shown for all PW@TiAl-SBA-15 samples with various HPW contents from 20 to 50 wt. %. An increase in the oscillation intensity at wavelengths of 890 cm⁻¹

and 962 cm⁻¹ is noted with an increased proportion of HPW, indicating the successful incorporation of HPW. These characteristic vibrations of HPW demonstrate the effective protonation of the TiAl-SBA-15 carrier, facilitating the attachment of active sites of PW⁻ to the TiAl-SBA-15 framework.

The XPS technique was used to determine the oxidation state of the active species in the photocatalyst. The Ti2p XPS spectra [Fig. 2a] exhibit a spin-orbit doublet with binding energies of 457.5 and 463.0 eV for Ti2p₃/₂ and Ti2p₁/₂, respectively, confirming the presence of Ti⁴⁺ ions in tetrahedral coordination. Additionally, Fig. 2b reveals two distinct regions for the binding energy of W4f, including the spin-orbit doublet at 35.5 eV corresponding to W4f₇/₂ and a second doublet at 37.7 eV for W4f₅/₂. These values are lower than those for W⁶⁺, which have binding energies of 36.8 eV (W4f₇/₂) and 39.0 eV (W4f₅/₂) [35,36]. The appearance of these lower energy values suggests partial reduction, like WO₂, compared to W⁶⁺. The presence of partially reduced forms of W⁶⁺ may enhance the efficiency of electron transfer in the catalytic oxidation of dibenzothiophene.

The XPS spectrum in the W 4f region (Fig. 2c) reveals the coexistence of two tungsten oxidation states, namely W⁶⁺ (W 4f₇/₂ ≈ 35.6 eV and W 4f₅/₂ ≈ 37.8 eV) and W⁵⁺ (W 4f₇/₂ ≈ 34.6 eV and W 4f₅/₂ ≈ 36.7 eV), in the catalyst. This result provides important evidence for electron transfer processes and oxygen vacancy formation during the oxidative desulfurization of dibenzothiophene into dibenzothiophene sulfone. The W⁵⁺ peaks shift toward lower binding energies by approximately 0.9–1.1 eV compared with those of W⁶⁺, indicating an increased electron density around the W atoms due to the partial reduction of W⁶⁺ to W⁵⁺. The conversion of W⁶⁺ to W⁵⁺ during the ODS process reflects active electron transfer and the generation of oxygen vacancies, which facilitate the

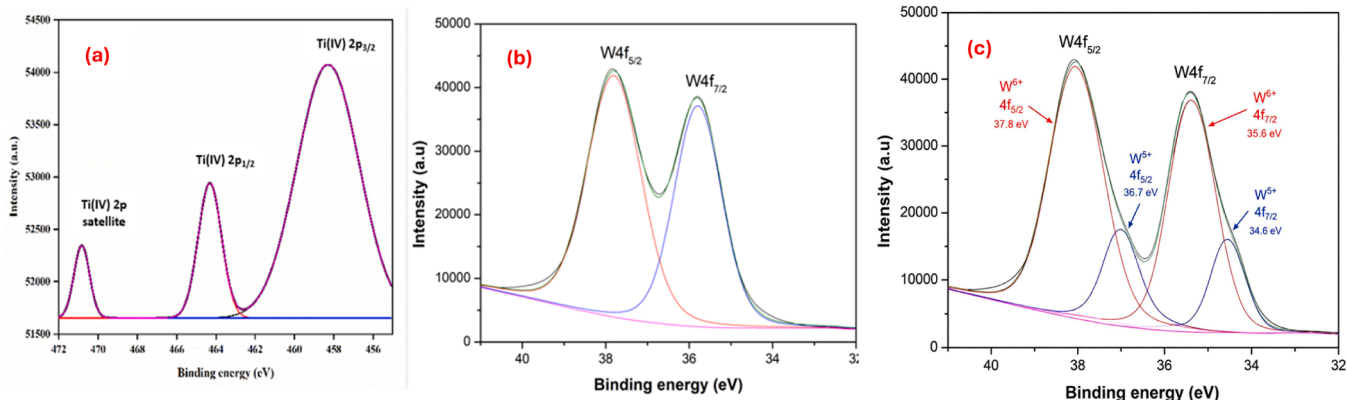


Fig. 2. XPS spectra for (a) Ti 2p, (b) W 4f before reaction and (c) W 4f reaction of 30% PW@TiAl-SBA-15 sample.

catalytic oxidation of DBT into DBTO₂.

In the H₂-TPR measurements, the reduction peaks reflect the stepwise reduction of POMs interacting with the support [Fig. S2]. For the PW@TiAl-SBA-15 catalyst system, tungsten species in the PW₁₂O₄₀³⁻ anion act as the primary redox - active centers, whereas Ti⁴⁺ species are generally difficult to reduce under conventional TPR conditions. The appearance of three reduction peaks at 356.1, 656.0, and 804.2 °C can be assigned as follows. The low temperature peak at 356.1 °C corresponds to the reduction of W⁶⁺ to W⁵⁺ [37,38], which is characteristic of readily reducible W⁶⁺ species. This peak is typically associated with well - dispersed PW₁₂O₄₀³⁻ clusters on the SBA-15 support, where terminal W=O species are exposed on the surface and weakly anchored. In addition, the presence of -H₃N⁺ groups and Ti-Al species within the SBA-15 framework contributes to stabilizing the POM structure while still allowing partial reduction at intermediate temperatures. This temperature region is associated with highly oxidative active sites and is crucial for the oxidative desulfurization reaction, particularly for the formation of peroxotungstate species.

The reduction peak at 656.0 °C can be attributed to the further reduction of tungsten species from W⁵⁺ to W⁴⁺. This higher-temperature reduction peak indicates the strong interaction between the POM species and the Ti-O-Al-O-Si framework, suggesting that a fraction of the POM is either structurally modified or deeply anchored within the mesoporous channels. The occurrence of this peak implies the coexistence of multiple tungsten oxidation states over this temperature range, which contributes

to enhanced thermal stability and improved redox cycling capability of the catalyst [39]. The high-temperature reduction peak observed at 804.2 °C corresponds to deep reduction of tungsten species from W⁴⁺ to metallic W⁰ or partially to W³⁺. Such a high reduction temperature reflects the complete decomposition of the POM framework and does not represent the catalytically active state under ODS reaction conditions. Instead, this peak defines the reduction limit of the material and further confirms the high thermal stability of the PW@TiAl-SBA-15 system, in which tungsten species are not readily reduced to lower oxidation states [40]. Accordingly, the low-temperature reduction peak (~356 °C) is commonly associated with the reversible W⁶⁺/W⁵⁺ redox cycle, which is regarded as the catalytically active redox couple in ODS reactions. In contrast, the higher-temperature reduction peaks correspond to tungsten species that are more strongly anchored to the support and therefore less accessible and less active under typical ODS operating conditions. Meanwhile, although Ti⁴⁺ species are not readily reducible, they play a crucial role in enhancing the anchoring and dispersion of tungsten species through the formation of Ti-O-W interfacial linkages within the PW@TiAl-SBA-15 system.

The morphological characteristics of TiAl-SBA-15 and 30% PW@TiAl-SBA-15 catalysts are depicted in Fig. 3. The SEM images [Fig. 3a and b] of TiAl-SBA-15 exhibit a uniform 2D cylindrical rod - like morphology, consistent with previous study [41]. Upon immobilizing HPW on the H₂N-TiAl-SBA-15 surface, the ordered uniform cylindrical structure is preserved. However, the SEM image of 30%

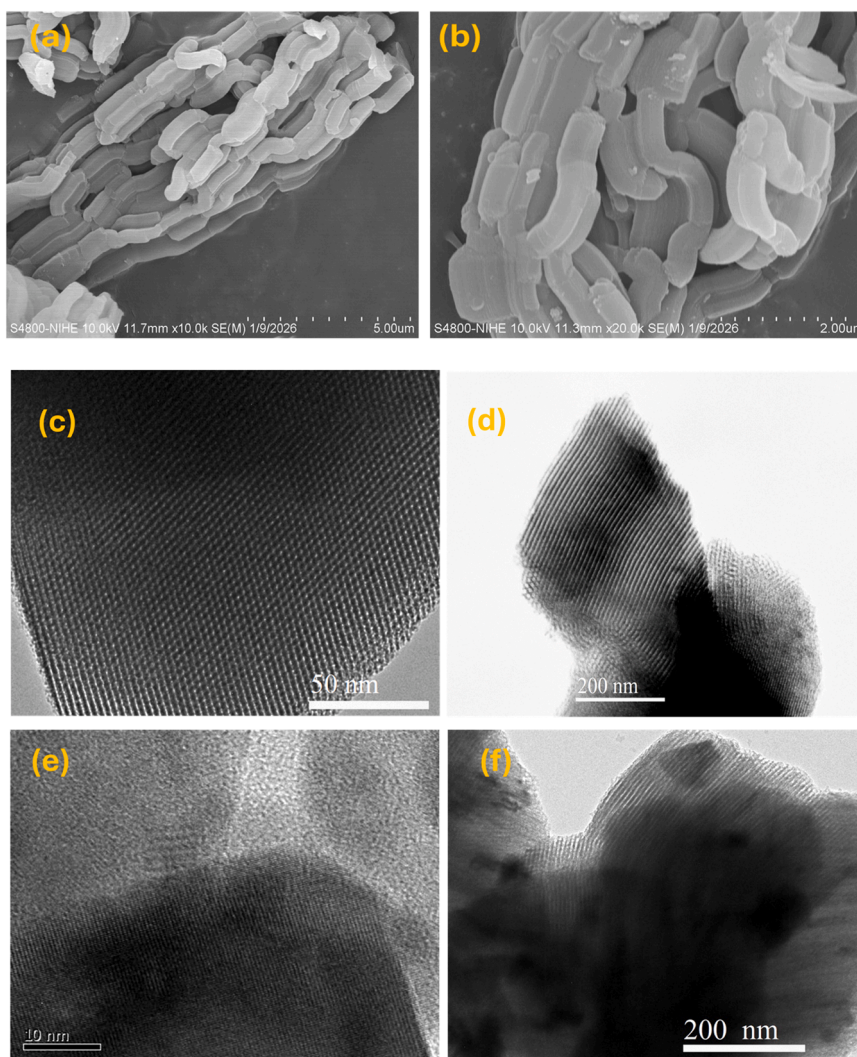


Fig. 3. (a, b) SEM images, and TEM images of (c, d) TiAl-SBA-15 and (e, f) 30% PW@TiAl-SBA-15 samples.

PW@TiAl-SBA-15 reveals a slightly agglomerated structure, attributed to the incorporation of HPW species into the titania - alumina - silica matrix. This morphology suggests the successful incorporation of HPW into the TiAl-SBA-15 framework.

TEM images of pure TiAl-SBA-15 and 30% PW@TiAl-SBA-15 catalysts are presented in Fig. 3c,d and e,f. The TEM of pure TiAl-SBA-15 exhibits a well - defined mesoporous structure with a honeycomb morphology characteristic of SBA-15 materials. In contrast, the 30% PW@TiAl-SBA-15 catalyst shows an intact mesoporous hexagonal arrangement with rod - shaped channels and a narrow size distribution. This TEM image confirms the uniform morphology of the PW@TiAl-SBA-15 photocatalyst, highlighting the high incorporation of HPW species within the hexagonal framework of TiAl-SBA-15.

The presence of all elements in the 30% PW@TiAl-SBA-15 catalyst was confirmed through EDX and EDX-mapping analysis [Fig. 4]. The EDX results reveal the presence of Si, O, Al, Ti, and P, along with the distribution of W within the catalyst. Additionally, mapping experiments indicate a well - dispersed W species within the TiAl-SBA-15, demonstrating a close attachment of tungsten to the titania - alumina - silica matrix at the nanoscale.

The nitrogen adsorption-desorption isotherms and pore size distribution curves for TiAl-SBA-15, ^+H_3N -TiAl-SBA-15 and 20–50% PW@TiAl-SBA-15 samples are presented in Fig. 5. Fig. 5. A shows that the N_2 adsorption-desorption isotherms of these samples are classified as Type-IV according to the IUPAC classification, with typical H_1 hysteresis loops observed at relative pressures (P/P_0) of 0.6–0.8. These results indicate a highly ordered mesoporous structure with a relatively narrow pore distribution in the cylindrical channels. However, the textural parameters, including Brunauer-Emmett-Teller specific surface area (S_{BET}), pore volume (V_{pore}) and pore diameter (D_{pore}), exhibited a slight decrease with increasing HPW content [Table 1]. That is, the specific surface area decreased from 627 m^2/g to 370.98 m^2/g as HPW content increased from 20% to 50% by weight. This reduction in surface area corresponded to a decrease in pore volume from 1.087 cm^3/g to 0.430 cm^3/g . Additionally, the pore size slightly decreased from 8.04 nm to 6.02 nm with an increase in HPW content from 20% to 50%. Table 2

3.2. Optical properties

The UV-Vis absorption spectra of TiAl-SBA-15 and 20–50%

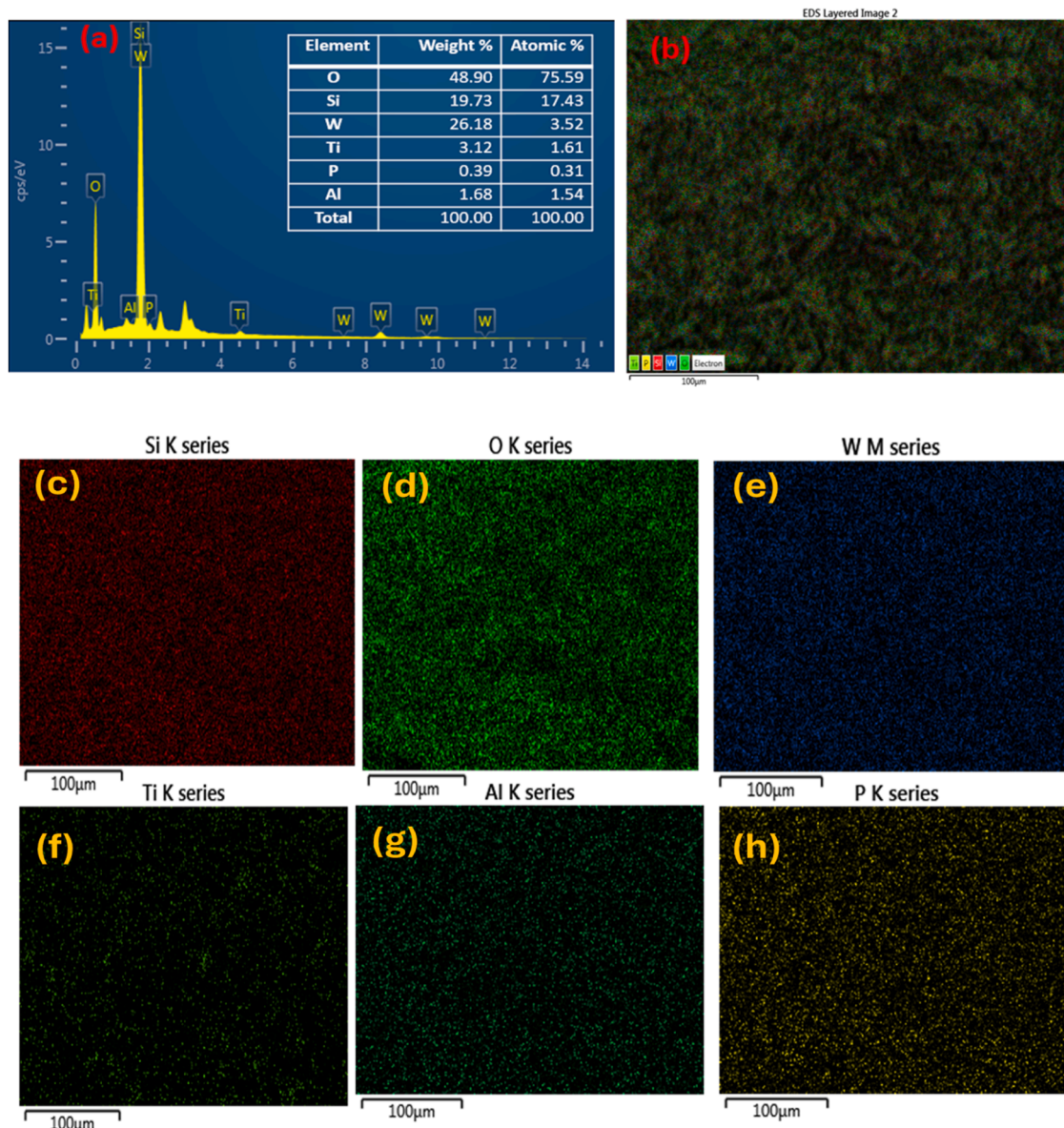


Fig. 4. (a) EDX spectrum and (b)-(h) Elemental mapping images of Si, O, W, Ti, Al, P in 30% PW@TiAl-SBA-15 sample.

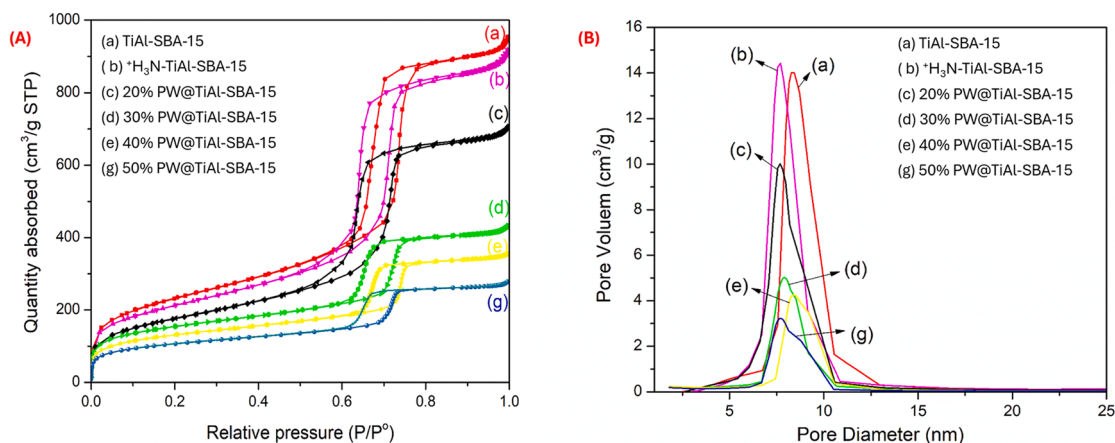


Fig. 5. (A) N₂ adsorption - desorption isotherms, and (B) Pore size distribution of TiAl-SBA-15, ⁺H₃N-TiAl-SBA-15 and 20–50% PW@TiAl-SBA-15 samples.

Table 1

Specific surface area, pore volume and pore diameter of TiAl-SBA-15, ⁺H₃N-TiAl-SBA-15 and 20–50% PW@TiAl-SBA-15 samples.

Sample	S _{BET} (m ² /g)	V _{pore} (cm ³ /g)	D (nm)
TiAl-SBA-15	822.09	1.47	8.04
⁺ H ₃ N-TiAl-SBA-15	754.47	1.41	7.72
20% PW@TiAl-SBA-15	627.00	1.09	7.35
30% PW@TiAl-SBA-15	535.03	0.66	6.47
40% PW@TiAl-SBA-15	451.61	0.55	6.19
50% PW@TiAl-SBA-15	370.98	0.43	6.02

PW@TiAl-SBA-15 samples are depicted in Fig. 6. It is known that pure WO₃ is a semiconductor with a strong absorption edge typically observed around 430 nm (E_g=2.88 eV) [42]. Upon anchoring HPW to the TiAl-SBA-15 surface, the absorption edge of the PW@TiAl-SBA-15 photocatalysts did not exhibit a significant shift, with the wavelength remaining in the range of 400–430 nm.

The band gap energy values were measured to be 3.06, 2.88, 2.86 and 2.89 eV for 20%, 30%, 40% and 50% HPW in TiAl-SBA-15, respectively (Eq. S2). The UV-Vis spectra indicate a noticeable shift towards the visible light region upon anchoring of the HPW group onto the TiAl-SBA-15 surface. Additionally, the band gap energy value decreases with increasing HPW content from 20 to 30%, remaining consistent when the HPW content reaches 50%. Furthermore, the UV-Vis results demonstrate that the composite effectively absorbs light in the visible region, generating more electron-hole pairs, which enhances photovoltaic performance.

Table 2

Comparison of ODS performance of HPW-based catalysts reported in the literature.

Catalyst	Sulfur compound concentration (ppm)	Oxidant	Light source	Temperature (°C)	Reaction time (min)	DBT conversion (%)	Reusability	Refs.
3DOM HPW/xCe-TiO ₂	500	H ₂ O ₂	None	60	40	99.8	6 cycles	[26]
Ce-UiO-66@5PW	1000	H ₂ O ₂	None	40	30	98.9	8 cycles	[50]
WO ₃ @ZrO ₂ -TiO ₂	500	H ₂ O ₂	None	Room temperature	80	100	4 cycles	[51]
PMO ₁₂ @ZIF-67	2000	H ₂ O ₂	None	70	120	94	4 cycles	[52]
(CTAB) ₃ H ₃ [PW ₉ V ₃ O ₄₀]/NH ₂ -Ti-SBA-15	1000	H ₂ O ₂	None	60	60	96.56	4 cycles	[53]
MoO ₃ -WO ₃ /SBA-15	200	H ₂ O ₂	None	Room temperature	180	97.50	5 cycles	[54]
W@NU-1000	1000	H ₂ O ₂	None	Room temperature	120	~100	5 cycles	[55]
PW4@MOF-808@SBA-15	1500	H ₂ O ₂	None	70	60	99.8	5 cycles	[56]
CuWO ₄ /SiO ₂	500	H ₂ O ₂	Visible light	Ambient temperature	70	98.6	4 cycles	[24]
PW@TiAl-SBA-15	300	H ₂ O ₂	Visible light	50	100	98.83	5 cycles	This work

3.3. Photocatalytic activity of catalysts in ODS of DBT

The photocatalytic activity of the prepared materials was evaluated under both dark conditions and natural light irradiation. The experiments were carried out under various conditions using 50 mL of DBT solution in *n*-octane and 50 mg of photocatalyst.

Fig. 7a presents the photocatalytic performance of Al-SBA-15, TiAl-SBA-15, and PW@TiAl-SBA-15 in the oxidative desulfurization of DBT. The Al-SBA-15 material predominantly acts as an adsorbent, where Al³⁺ species function as both Lewis and Brønsted acid sites. These active centers interact with the electron-rich sulfur atom in DBT molecules [43], resulting in a removal efficiency of 37% after 100 min, mainly through adsorption. In comparison, the TiAl-SBA-15 catalyst exhibits a significantly higher efficiency of 75%, indicating that the incorporation of titanium species markedly enhances photocatalytic activity. This improvement is attributed to the generation of electron-hole pairs under light irradiation, which facilitates the formation of reactive oxygen species responsible for DBT oxidation. Notably, the PW@TiAl-SBA-15 catalyst demonstrates superior performance due to the synergistic interaction between Ti active sites and polyoxometalate species. Phosphotungstic acid not only promotes the efficient activation of H₂O₂ but also acts as an effective electron acceptor, thereby suppressing charge recombination and enhancing the generation of reactive radical species. Consequently, complete DBT conversion (100%) is achieved over the PW@TiAl-SBA-15 catalyst.

As shown in Fig. 7b, the desulfurization rate varies with the HPW loading in the catalyst. Increasing the HPW content from 20% to 30%

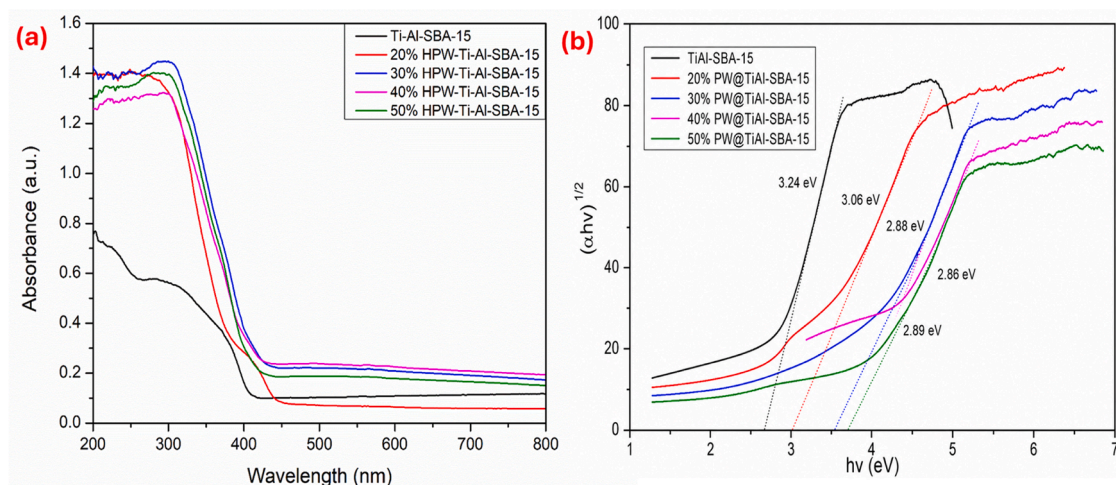


Fig. 6. (a) UV-Vis absorption spectra and (b) E_g diagram of TiAl-SBA-15 and 20–50% PW@TiAl-SBA-15 samples.

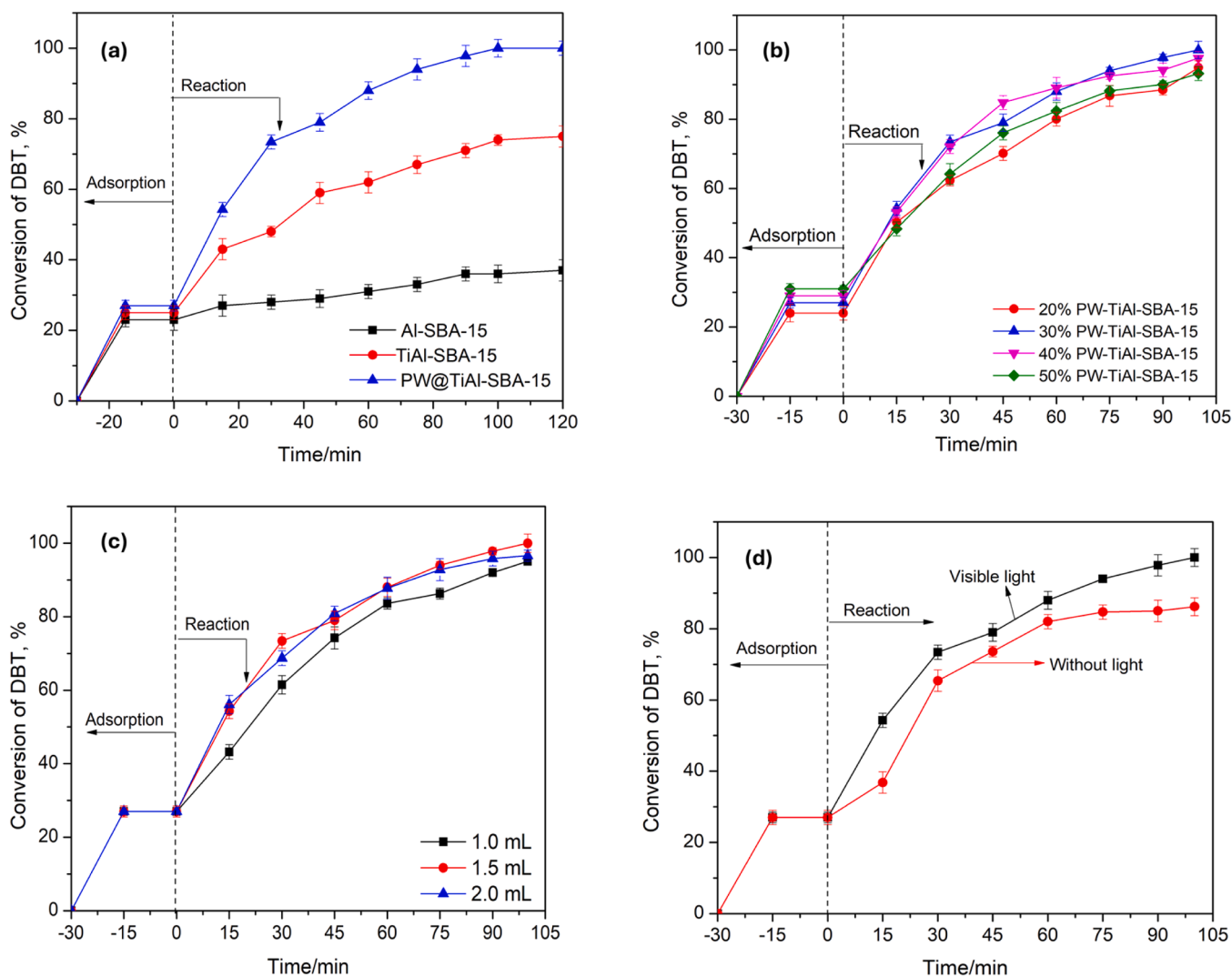


Fig. 7. Photocatalytic oxidative desulfurization activity of (a) Al-SBA-15, TiAl-SBA-15 and 30%PW@TiAl-SBA-15; (b) PW@TiAl-SBA-15 photocatalyst with different wt.% of HPW; (c) 30%PW@TiAl-SBA-15 photocatalyst with different concentration of H_2O_2 ; and (d) 30%PW@TiAl-SBA-15 under visible light and without visible light. (Reaction conditions: $m_{\text{catalysts}}=50$ mg; $V_{\text{oil fuel}}=50$ mL, $V_{H_2O_2}=1.5$ mL and 50°C).

leads to a noticeable enhancement in catalytic performance, with the DBT removal efficiency improving from 94.8% to complete conversion

at 50°C . However, a further increase in HPW loading to 40% results in a slight decline in DBT conversion to 97.4% under the same conditions.

This decrease can be attributed to the reduction in specific surface area and pore volume of the PW@TiAl-SBA-15 materials at higher PW loadings (40–50%), which limits the accessibility of active sites. Additionally, the ODS of DBT exhibits a rapid initial stage upon the addition of 1.0 mL H_2O_2 , followed by a slower oxidation process in the later stages. This behavior suggests that the interaction between catalytic active sites and sulfur-containing compounds is more effective at the beginning of the reaction, thereby facilitating faster oxidation of DBT, while the reaction rate gradually decreases as the process proceeds.

Fig. 7c illustrates the impact of varying hydrogen peroxide concentrations on the conversion of DBT. The data indicates a notable change in DBT conversion rates corresponding to different H_2O_2 vol. When the H_2O_2 concentration was increased from 1.0 mL to 1.5 mL, there was a significant rise in DBT conversion, from 43.2% to 54.3% within the first 15 min, eventually reaching 100% after 100 min. This increase can be attributed to the generation of more $\cdot\text{OOH}$ radicals from H_2O_2 , enhancing the reaction process and, consequently, the conversion rate. However, an interesting observation was made upon further increasing the H_2O_2 vol to 2.0 mL. Contrary to expectations, the conversion rate decreased sharply, dropping from 100% to 96.65% after 100 min. This decrease can be explained by the accelerated decomposition of H_2O_2 at higher concentrations, which leads to an increased concentration of H^+ ions in the catalyst system. These protons can attack the oxygen atoms in the $\text{W}=\text{O}$ bonds, impeding the formation of peroxotungstate $\text{W}(\text{O}_2)^{2-}$ intermediate states. Consequently, the formation of the hydroperoxytungstate group diminishes, adversely affecting the oxidative desulfurization activity of DBT [44]. Furthermore, an excessively high concentration of H_2O_2 can lead to the saturation of the active sites of the catalyst, thus reducing the overall reaction rate [45].

The oxidative desulfurization of DBT over the PW@Ti-Al-SBA-15 catalyst proceeds effectively under both dark and visible-light conditions; however, the presence of visible light significantly enhances the catalytic performance. In the absence of light, the DBT conversion reaches only 86.2% (Fig. 7d), indicating that the reaction predominantly follows a conventional catalytic oxidation pathway. In this case, phosphotungstic acid activates H_2O_2 to generate peroxo species, which are responsible for the oxidation of DBT.

3.4. Kinetic study of photocatalytic oxidative degradation of DBT over PW@TiAl-SBA-15

Based on the optimized experimental conditions (50 mL DBT in *n*-octane, 1.0 mL H_2O_2 , 50 mg PW@TiAl-SBA-15 catalyst, temperatures of 40, 50, and 60 °C, and initial DBT concentrations of 300, 500, and 600 ppm), the photocatalytic oxidative degradation of DBT under visible-

light irradiation can be well described by a pseudo-first-order kinetic model, as expressed in Eq. S3. The kinetic plots shown in Figs. 8b and 9b exhibit excellent linearity with correlation coefficients ($R^2 \approx 0.99$) under various concentrations and temperatures, confirming the validity of the pseudo-first-order model. For instance, the rate constant at 50 °C and an initial DBT concentration of 300 ppm is determined to be 0.039 min^{-1} .

An increase in temperature from 40 to 60 °C significantly enhances the DBT conversion over the entire reaction time. This behavior can be explained by the exponential increase in the reaction rate constant according to the Arrhenius equation, which promotes more effective collisions between DBT molecules and reactive oxidizing species. Additionally, higher temperatures improve mass transfer and facilitate the diffusion of DBT into the porous structure of the catalyst, thereby increasing the accessibility of active sites.

Compared with previous studies, DBT conversion efficiencies of approximately 90% for 7.5Ti-Al-SBA-15 [11], 98.66% for 30%Ag@AgBr/Al-SBA-15 [48], and nearly 100% for PW-H₃N⁺-SBA-15 at 90 °C [37] have been reported. Notably, the present PW@TiAl-SBA-15 system achieves comparable or superior performance under milder conditions. However, at 60 °C, the system reaches equilibrium more rapidly, which may lead to the non-productive decomposition of H_2O_2 and a decrease in oxidation selectivity. Therefore, 50 °C is identified as the optimal temperature for efficient DBT conversion in this system.

In contrast, if the reaction follows a second-order kinetic model, it can be expressed as Eq.S4. However, the calculated results indicate that the second-order kinetic model does not adequately describe the photocatalytic oxidative desulfurization of DBT (Figs. S3 and S4). Specifically, at 50 °C and an initial DBT concentration of 300 ppm, a relatively low correlation coefficient ($R^2 = 0.692$) is obtained. Therefore, the second-order kinetic model is not suitable for describing the photocatalytic oxidation of DBT under visible-light irradiation.

The Arrhenius plot based on the pseudo-first-order model is shown in Fig. S5 (Eqs. S5 và S6). The apparent activation energy (E_a) is calculated from the slope of the linear fitting, yielding a value of 28.143 $\text{kJ}\cdot\text{mol}^{-1}$. This relatively low activation energy for a photocatalytic oxidative process suggests that the reaction proceeds readily with a reduced energy barrier and is not strongly limited by kinetic constraints. This finding further confirms the synergistic effect between photocatalysis and catalytic oxidation, where the generation of highly reactive radical species facilitates the reaction and enhances the overall kinetics.

Notably, the apparent activation energy ($E_a \approx 28.1 \text{ kJ}\cdot\text{mol}^{-1}$) obtained in this study is significantly lower than those reported for conventional ODS systems, such as $\text{MoO}_3/\text{Al}_2\text{O}_3$ ($\approx 33 \text{ kJ}\cdot\text{mol}^{-1}$) [46], WO_3/SnO_2 ($\approx 54.8 \text{ kJ}\cdot\text{mol}^{-1}$) [47], and 30%Ag@AgBr/Al-SBA-15 ($\approx 48.93 \text{ kJ}\cdot\text{mol}^{-1}$) [48]. This lower activation energy indicates that DBT

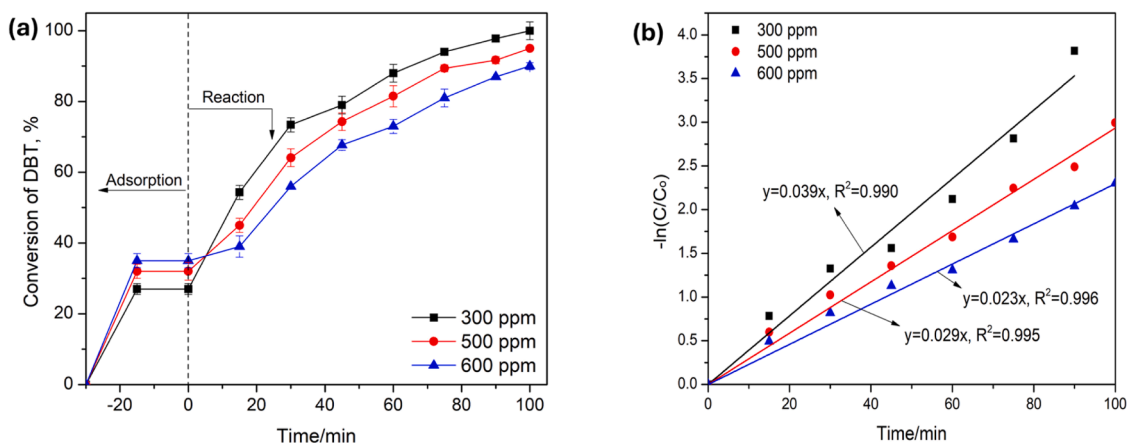


Fig. 8. (a) Photocatalytic oxidative degradation of DBT over 30%PW@TiAl-SBA-15 at various initial concentrations; (b) corresponding pseudo-first-order kinetic plots. (Reaction conditions: model oil volume = 50 mL, H_2O_2 volume = 1.0 mL, catalyst dosage = 50 mg, reaction temperature = 50 °C under visible-light irradiation).

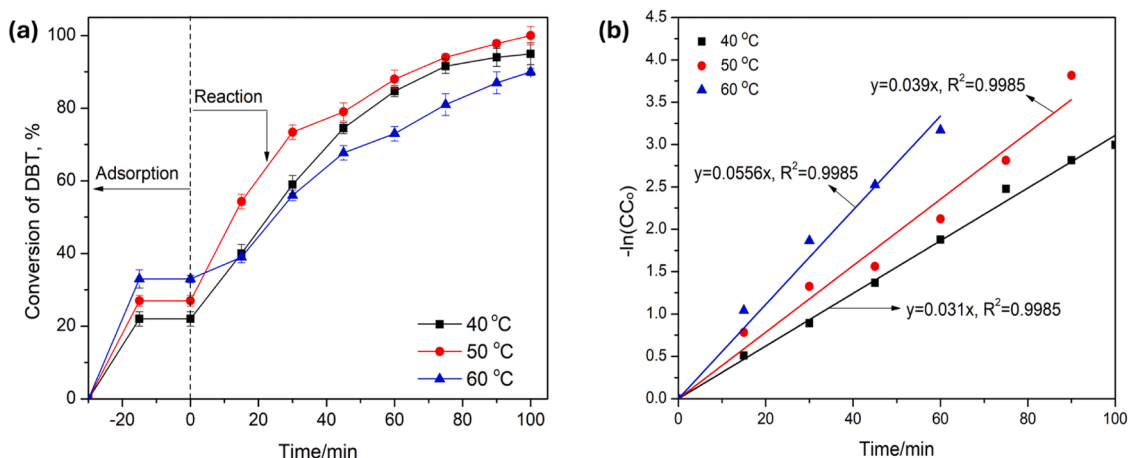


Fig. 9. (a) Photocatalytic oxidative degradation of DBT over 30%PW@TiAl-SBA-15 at various temperatures; (b) corresponding pseudo-first-order kinetic plots. (Reaction conditions: model oil volume = 50 mL, H_2O_2 volume = 1.0 mL, catalyst dosage = 50 mg, initial DBT concentration = 300 ppm, under visible-light irradiation).

oxidation over PW@TiAl-SBA-15 proceeds more efficiently with a reduced energy barrier. The enhanced performance can be attributed to the synergistic interaction between Ti species and polyoxometalates, which improves charge separation and promotes the generation of reactive oxygen species under visible-light irradiation. Consequently, the reaction follows a more efficient photocatalytic pathway compared to conventional thermally driven catalytic systems.

3.5. Photocatalytic reaction mechanism of PW@TiAl-SBA-15 in ODS of DBT

To gain deeper insight into the active species involved in DBT conversion over the PW@TiAl-SBA-15 catalyst, radical scavenging experiments were carried out. In this study, 1,4-benzoquinone (BQ), dimethyl sulfoxide (DMSO), isopropyl alcohol (IPA), and disodium ethylenediaminetetraacetate (EDTA-2Na) were employed as selective quenchers for superoxide radicals ($\cdot O_2^-$), hydroperoxyl ($\cdot OOH$), hydroxyl radicals ($\cdot OH$), and photogenerated holes (h^+), respectively. As shown in Fig. 10, the DBT conversion decreased dramatically upon the addition of BQ, dropping from 99.80% to 27.60%, indicating a dominant role of

superoxide-related species. In addition, quenching of $\cdot OH$ radicals by IPA also led to a noticeable decrease in DBT conversion to 56.50%, whereas the introduction of EDTA-2Na caused only a marginal reduction in DBT conversion (94.30%).

These radical trapping experiments clearly demonstrate that peroxy/superoxide species ($\cdot OOH/\cdot O_2^-$) act as mild yet highly effective oxidants and constitute the primary reactive species throughout the selective photocatalytic oxidative desulfurization of dibenzothiophene over PW@TiAl-SBA-15, while hydroxyl radicals play a secondary role. Photogenerated holes (h^+) are not the main oxidizing agents in the ODS process. Instead, h^+ primarily facilitate charge separation by suppressing electron-hole recombination, thereby indirectly promoting the formation of peroxotungstate species and $\cdot OOH/\cdot O_2^-$ radicals, which are responsible for the selective oxidation of sulfur-containing compounds.

The decrease in ODS efficiency (52.70%) upon the addition of DMSO demonstrates that $\cdot OOH$ radicals participate in the reaction mechanism. However, the inhibition effect was lower than that observed when using BQ as a scavenger for $O_2^{\cdot -}$ radicals. This result indicates that $O_2^{\cdot -}$ is the dominant reactive oxygen species, whereas $\cdot OOH$ mainly acts as an intermediate or auxiliary oxidizing species in the oxidation pathway.

The reaction mechanism is described by the following elementary steps. Under visible-light irradiation, the Ti-Al-modified SBA-15 framework and the phosphotungstate species are photoactivated:



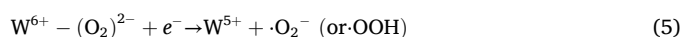
The photogenerated electrons are rapidly transferred to the excited PW clusters, leading to the reduction of tungsten centers:



Simultaneously, photogenerated electrons participate in the activation of hydrogen peroxide to form peroxo-tungstate species [49]:



The peroxotungstate species further interact with electrons to generate reactive superoxide/peroxyl radicals:



The facile reduction of W^{6+} to W^{5+} enables rapid trapping of photogenerated electrons, which effectively suppresses electron-hole (e^-/h^+) recombination and enhances the concentration of oxidative reactive species.

The peroxo-tungstate moieties, such as $[WO_m(O_2)_2]^{2-}$ or surface-

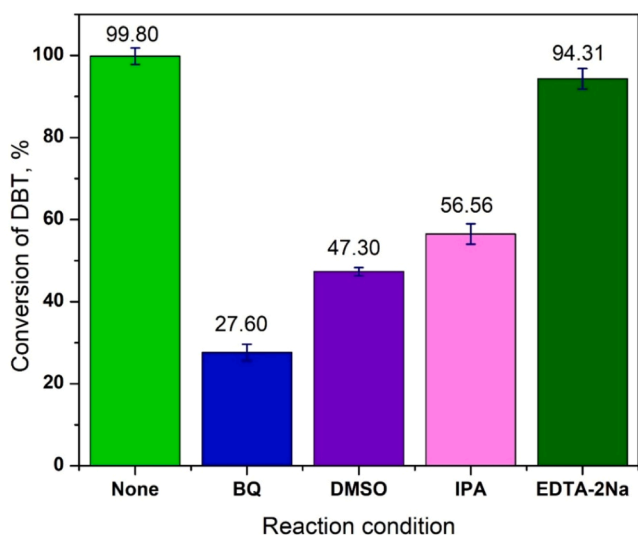


Fig. 10. Identification of reactive oxygen species: Photocatalytic conversion efficiency of DBT under different radical-scavenging conditions. (Conditions: 50 mg of 30% PW@TiAl-SBA-15 photocatalyst; scavenger=3.5 mM; DBT = 300 ppm; reaction temperature of 50 °C under visible light irradiation).

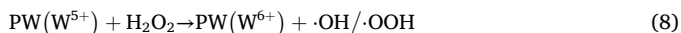
associated $W=O\cdots OOH$ species, act as selective oxidation centers for dibenzothiophene (DBT), promoting its conversion to dibenzothiophene sulfoxide (DBTO):



Subsequently, DBTO undergoes further oxidation to form dibenzothiophene sulfone (DBTO₂):



Regeneration of the active PW redox centers is achieved through oxidation of W^{5+} species by hydrogen peroxide:



Alternatively, molecular oxygen or peroxo ligands can also contribute to the reoxidation of reduced tungsten species:



The proposed photocatalytic redox mechanism for the oxidative desulfurization of dibenzothiophene on the PW@TiAl-SBA-15 catalyst is shown in Fig. 11.

Accordingly, the transformation of W^{6+} to W^{5+} in the PW@TiAl-SBA-15 system does not represent permanent reduction of tungsten species but rather a transient electron-buffering process. The W^{5+} species are generated mainly through photoinduced electron transfer from Ti-related centers or via ligand-to-metal charge transfer within the polyoxometalate framework, and are rapidly reoxidized during H_2O_2 activation. This dynamic W^{6+}/W^{5+} redox cycle, rather than the accumulation of reduced tungsten species, underpins the high photocatalytic ODS activity. These findings are consistent with the facile W^{6+}/W^{5+} redox behavior evidenced by low-temperature H_2 -TPR reduction features, as well as with the preferential formation of peroxotungstate intermediates that selectively oxidize C-S bonds.

DBT in the model fuel and the sulfur-containing compounds generated during the desulfurization process were analyzed by GC/MS. Prior to the photocatalytic oxidation reaction, DBT was the only sulfur-containing species detected [Fig. 12a]. After the oil phase was extracted using silica gel as an adsorbent and further analyzed, a substantial amount of DBTO₂ was identified [Fig. 12b]. These results demonstrate that DBT was oxidized to the more polar DBTO₂ species in the oil phase during the photocatalytic oxidative desulfurization process, ultimately achieving deep desulfurization.

3.6. The recyclability and stability of PW@TiAl-SBA-15 catalyst

Catalyst stability is a crucial aspect of the photocatalytic process. To assess the stability of the 30% PW@TiAl-SBA-15 catalyst, it was subjected to a series of regeneration cycles. Post-reaction, the catalyst was recovered through centrifugation, followed by thorough washing with distilled water and ethanol.

As depicted in Fig. S6a, the DBT conversion efficiency exhibited a

marginal decline across successive regeneration cycles but remained impressively above 98.83% even after five cycles. This slight reduction in photocatalytic activity could be attributed to minor catalyst loss during the experimental procedure. Nevertheless, the consistent conversion rate of approximately 99% throughout the tests strongly indicates that the 30% PW@TiAl-SBA-15 catalyst possesses robust photocatalytic stability, maintaining its effectiveness over multiple uses. Furthermore, the photocatalyst after multiple reaction cycles exhibits structural and spectroscopic characteristics that are essentially identical to those of the pristine PW@TiAl-SBA-15 catalyst. The FT-IR spectra of $PW_{12}O_{40}^{3-}@NH_4^+-TiAl-SBA-15$ before and after reaction are presented in Fig. S6b. The characteristic vibrational bands of the Keggin-type heteropolyanion $PW_{12}O_{40}^{3-}$ are clearly observed in the region of 700–1100 cm^{-1} , confirming the successful immobilization of the active species onto the functionalized support. Specifically, four typical absorption bands can be assigned to the stretching vibrations of P-O_a (~1080 cm^{-1}), terminal W=O_t (~951 cm^{-1}), and bridging W-O_b-W (~892 cm^{-1}) and W-O_c-W (~810 cm^{-1}), respectively. These bands are still present after the reaction, indicating that the primary Keggin structure remains largely intact during the catalytic process, while the X-ray diffraction patterns still reveal the well-defined two-dimensional hexagonal mesostructure of SBA-15. These results demonstrate the excellent cycling performance and structural stability of the catalyst, which are highly advantageous for practical applications and long-term continuous operation.

The FT-IR spectra shown in Fig. S7a,b reveal significant changes in the characteristic vibrational bands of dibenzothiophene and dibenzothiophene sulfone after the oxidation process over the PW@TiAl-SBA-15 catalyst surface, thereby confirming the successful conversion of DBT into the corresponding sulfone. In Fig. S7a, the FTIR spectrum of DBT exhibits characteristic vibrations of the aromatic framework, including the absorption band at approximately 3050–3100 cm^{-1} assigned to the aromatic $\nu(C-H)$ stretching vibration, the region at 1450–1600 cm^{-1} corresponding to the $\nu(C=C)$ vibrations of the aromatic rings, the signal around 1000–1100 cm^{-1} associated with the aromatic $\delta(C-H)$ in-plane bending vibration, and the band at 720–760 cm^{-1} attributed to the aromatic $\gamma(C-H)$ out-of-plane bending vibration.

After the reaction, the FT-IR spectrum of dibenzothiophene sulfone in Fig. S7b still retains the characteristic vibrations of the aromatic framework, indicating that the benzene ring structure remained intact during the oxidation process. However, two new absorption bands appeared at approximately ~1150 cm^{-1} ($\nu_s(S=O)$) and ~1330 cm^{-1} ($\nu_{as}(S=O)$), which are characteristic of the sulfone O=S=O bond. The simultaneous appearance of the symmetric and asymmetric stretching vibrations of the S=O group confirms that the sulfur atom in DBT was completely oxidized into the sulfone form.

The N_2 adsorption-desorption isotherms of the TiAl-SBA-15 sample before and after the reaction [Fig. S7c] exhibit characteristic features of mesoporous materials. A distinct adsorption-desorption hysteresis loop is observed in the relative pressure region of $P/P_0 \approx 0.6-0.8$, indicating the presence of a relatively uniform and ordered mesoporous channel

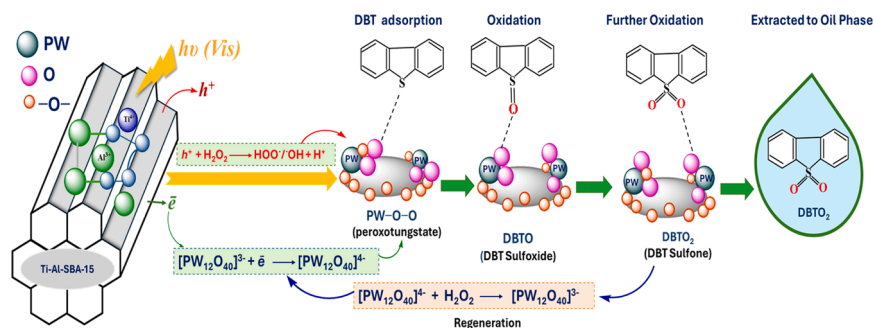


Fig. 11. Proposed photocatalytic redox mechanism for dibenzothiophene oxidative desulfurization over the PW@TiAl-SBA-15 catalyst, illustrating H_2O_2 activation, W^{6+}/W^{5+} redox cycling, and the generation of reactive oxygen species under visible-light irradiation.

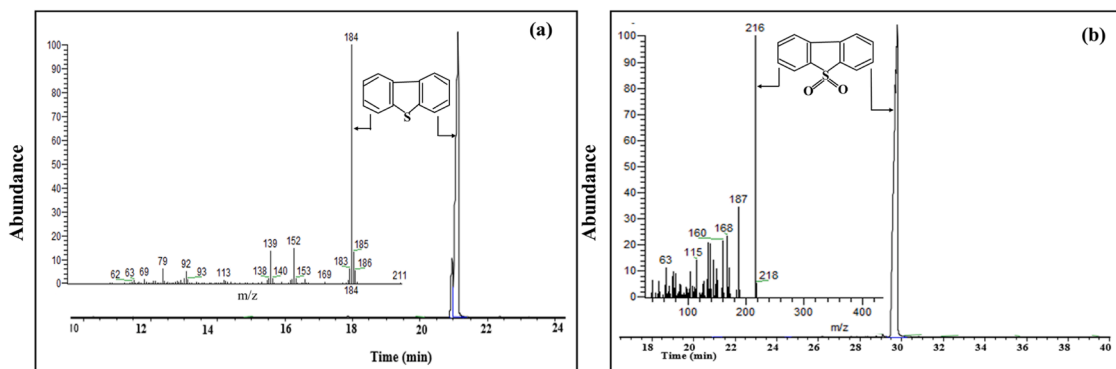


Fig. 12. GC-MS spectra of model fuel (a) before and (b) after reaction.

system characteristic of the SBA-15 structure. This result confirms that the mesoporous framework of the material was largely preserved after the ODS process. However, the hysteresis loop area became narrower compared with that of the fresh sample, suggesting a decrease in the specific surface area and pore volume ($S_{\text{BET}} \approx 460 \text{ m}^2 \text{ g}^{-1}$, $V_{\text{pore}} \approx 0.56 \text{ cm}^3 \text{ g}^{-1}$). This phenomenon can be attributed to the deposition or adsorption of dibenzothiophene sulfone within the mesoporous channels of the catalyst.

The pore size distribution results shown in Fig. S7d reveal that both samples possess a narrow pore size distribution centered mainly at approximately 6.4 nm, reflecting the high uniformity of the SBA-15 mesoporous system. After the reaction, the pore size distribution peak remained located in a similar size region, indicating that the mesoporous framework of the catalyst was not destroyed under the reaction conditions. Nevertheless, the intensity of the pore size distribution peak for the used catalyst decreased significantly, accompanied by a lower pore volume compared with the fresh sample. This observation suggests that a portion of the pores was occupied by DBT sulfone or intermediate products adsorbed on the catalyst surface. The reduction in pore volume therefore provides indirect evidence for the formation and retention of oxidation products within the mesoporous channels of the catalyst.

After the ODS reaction, the BET surface area and pore volume of the PW@TiAl-SBA-15 catalyst decreased significantly, which may be attributed to the deposition of DBT sulfone inside the mesoporous channels. However, the pore diameter decreased only slightly, indicating that the ordered mesoporous structure of the catalyst was largely maintained after the reaction.

Compared with previously reported POM/SBA-15 catalysts, the 30% PW@TiAl-SBA-15 photocatalyst demonstrates substantially superior ODS performance under significantly milder reaction conditions. Nearly complete DBT conversion is achieved at 50 °C under visible-light irradiation, whereas most conventional HPW/SBA-15-based systems typically require elevated temperatures ($\geq 60 \text{ °C}$) and operate in the absence of light. This enhanced activity is attributed to the synergistic coupling between peroxotungstate redox chemistry and efficient visible-light-induced charge separation within the Ti-modified SBA-15 framework. In addition, strong ionic immobilization of PW species via $-\text{NH}_3^+$ functional groups effectively suppresses HPW leaching, resulting in excellent catalytic recyclability and long-term structural stability.

4. Conclusions

This study successfully demonstrated the synthesis, characterization, and photocatalytic application of PW@TiAl-SBA-15 for the oxidative desulfurization of dibenzothiophene. The incorporation of HPW into the TiAl-SBA-15 framework significantly enhanced visible-light-driven photocatalytic activity through the synergistic $\text{W}^{6+}/\text{W}^{5+}$ redox cycle. Under optimized conditions, the catalyst achieved a DBT conversion of up to 100%. The dependence of photocatalytic performance on HPW

loading highlights the importance of balancing active component content, as excessive HPW reduced surface area and pore volume, thereby affecting catalytic efficiency. In addition, the effect of H_2O_2 concentration revealed that moderate levels favor DBT oxidation, whereas excessive amounts suppress performance, emphasizing the need for reagent optimization. Notably, the 30% PW@TiAl-SBA-15 catalyst exhibited excellent stability, maintaining over 98.83% conversion after five regeneration cycles. Overall, this work provides valuable insights into the design of efficient, stable, and reusable photocatalysts for oxidative desulfurization, offering promising potential for environmentally sustainable fuel purification under visible-light irradiation.

Data availability: No data were generated or analyzed during the current study.

CRediT authorship contribution statement

Xuan Nui Pham: Writing – review & editing, Supervision, Project administration, Methodology, Funding acquisition, Data curation, Conceptualization. **Van Huan Doan:** Writing – original draft, Validation, Formal analysis, Data curation. **Tien-Dung Cong:** Validation, Investigation, Formal analysis, Data curation. **Thanh-Hai Ngo:** Writing – original draft, Validation, Investigation, Formal analysis, Data curation.

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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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.mcat.2026.116132](https://doi.org/10.1016/j.mcat.2026.116132).

Data availability

The authors do not have permission to share data.

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