

MJAS2020

by Leny Yuliaty

Submission date: 27-Jul-2022 03:53PM (UTC+0800)

Submission ID: 1875756507

File name: Methylene_Blue_by_Adsorption_and_Photocatalytic_Degradation.pdf (2.22M)

Word count: 6925

Character count: 36541

ROLE OF VANADIA AND TITANIA PHASES IN THE REMOVAL OF METHYLENE BLUE BY ADSORPTION AND PHOTOCATALYTIC DEGRADATION

(Peranan Fasa Vanadia dan Titania dalam Penyingkiran Metilena Biru Melalui Penjerapan dan Degradasi Fotokatalisis)

Pei Wen Koh^{1,2}, Cheng Yee Leong², Leny Yuliati^{2,3}, Hadi Nur², Siew Ling Lee^{2*}

¹Department of Chemistry, Faculty of Science

²Centre for Sustainable Nanomaterials, Ibnu Sina Institute for Scientific and Industrial Research
Universiti Teknologi Malaysia, 81300 Johor Bahru, Malaysia

³Ma Chung Center for Photosynthetic Pigments,
Universitas Ma Chung, Malang 65151, Indonesia

*Corresponding author: sllee@ibnusina.utm.my

40

Received: 18 July 2019; Accepted: 20 July 2020; Published: 10 December 2020

Abstract

Total removal of methylene blue (MB) over vanadia (V_2O_5)-modified titania (TiO_2) composite demonstrated that the V_2O_5 and TiO_2 phases played a vital role in the adsorption and photodegradation of MB, respectively. The 10 mol% of V_2O_5 -modified TiO_2 (10V- TiO_2) showed the highest removal of MB, i.e., 26- and 2-folds better adsorption capacity than that of undoped TiO_2 and V_2O_5 , respectively. The presence of surface hydroxyl, and the highest amount of V^{5+} species in V- TiO_2 could be responsible for the high adsorption of MB. V_2O_5 induced anatase to rutile phase transformation and shifted absorption properties of TiO_2 to the visible light region. Considering the rutile phase has lower bandgap energy (3.0 eV), its presence in the sample has enhanced the photodegradation of MB. The photodegradation of MB followed pseudo-second-order reaction. The reusability test elucidated that the photodegradation performance of 10V- TiO_2 was improved by 30-folds after the second cycle, with total MB removal due to the exposure of more TiO_2 to MB.

Keywords: vanadia, titania, methylene blue, adsorption, photocatalyst, photodegradation

Abstrak

Penyingkiran metilena biru (MB) secara keseluruhan oleh komposit titania (TiO_2) yang diubahsuai dengan vanadia (V_2O_5) menunjukkan bahawa fasa V_2O_5 dan TiO_2 masing-masing memainkan peranan penting dalam penjerapan dan fotodegradasi MB. TiO_2 yang diubahsuai dengan 10 mol% V_2O_5 (10V- TiO_2) menunjukkan penyingkiran MB yang tertinggi, iaitu 26- dan 2-kali ganda kapasiti penjerapan yang lebih baik daripada TiO_2 dan V_2O_5 yang tidak didopkan. Kewujudan hidrosil di permukaan, liang, dan jumlah spesis V^{5+} tertinggi dalam 10V- TiO_2 menyumbang kepada penjerapan MB yang tinggi. V_2O_5 mendorong transformasi fasa anatase ke rutil dan sifat-sifat penyerapan TiO_2 beralih ke rantau cahaya nampak. Memandangkan fasa rutil mempunyai tenaga jurang jalur yang lebih rendah (3.0 eV), kewujudannya dalam sampel telah meningkatkan prestasi fotodegradasi MB. Fotodegradasi MB mengikuti tindak balas tertib pseudo-kedua. Ujian kebolehgunaan tersebut membuktikan bahawa prestasi

fotodegradasi 10V-TiO₂ telah ditingkatkan sebanyak 30-kali ganda selepas kitaran kedua kerana lebih banyak TiO₂ terdedah kepada MB.

Kata kunci: vanadia, titania, metilena biru, penjerapan, fotokatalis, fotodegradasi

Introduction

Soil and water contamination by dye-containing effluents are serious environmental issues. The release of these coloured compounds into the drainage system has significantly impacted human and aquatic lives due to their toxicity. Although many technologies have been developed to treat dye-containing effluent at an acceptable level before drainage, there is no single process capable of adequately treating these dye-containing wastewaters. It was suggested that a combination of different techniques would be a better solution to remove the dyes [1, 2]. Compared to the conventional biological physicochemical method, it is undeniable that adsorption is a superior method established for the removal of dye due to its simplicity in design, efficiency, and ability to treat dye larger quantities [3]. A good adsorbent should have high selectivity and adsorption capacity for the targeted adsorbate. However, in many cases, surface modification using an expensive surfactant, chemical, or heat treatment is always applied to solve the limitations of the surface functional group of adsorbents [4]. Another shortcoming of the adsorption method is associated with the formation of secondary pollution following the adsorption process. Photocatalysis appears to be a promising green technology approach to address this problem compared to conventional treatments such as flocculation, coagulation, and adsorption, which often result in secondary pollution [5, 6]. Photocatalysis is capable of fully mineralising toxic dye to non-toxic anionic compounds. However, its usage is only applicable to trace amount of dye-containing wastewater.

Among many semiconductor photocatalysts, titanium dioxide (TiO₂) has gained considerable attention due to its high activity, high light-illumination stability, non-toxic properties, and low price [7]. However, its low surface area has limited its adsorption and photocatalytic

degradation efficiency under ultraviolet (UV) light. Recently, comprehensive review and studies on the effectiveness of incorporating TiO₂ on porous adsorbents had been reported [8-10]. The catalytic performance of TiO₂ can be improved by loading TiO₂ onto various supporting adsorbents. Other drawbacks of TiO₂ photocatalyst include high recombination rate of the electron-hole, high bandgap energy, and inactivity under visible light that affected its application under sunlight. A standard method used to solve the problems above is the modification of TiO₂ via transition metal doping. Transition metal doping appears to be one of the most effective approaches to reduce the rate of electrons and holes recombination [1, 11-13]. Visible light-driven vanadia-doped titania photocatalysts in pure anatase phase have been reported [14, 15]. The enhanced photocatalytic behaviour was attributed to the highly dispersed vanadia in the TiO₂ crystallite, which successfully reduced the bandgap energy and increased the ability to absorb visible light.

Nguyen et al. reported that 10% vanadia-doped TiO₂ (V-TiO₂) is an excellent adsorbent for decolourisation of methylene blue (MB) [16]. This material possessed anatase and a negligible percentage of brookite phases. It was claimed that the good interaction between vanadia-doped TiO₂ and the dye molecules as well as the increased oxidation states of Ti, V, and O have contributed to the excellent adsorption ability of the material, resulting in the removal of 91.6% MB after 2 hours reaction time [16]. The usage of V-TiO₂ as a photocatalyst has been widely reported. In the current study, we present new insight into the role of the respective vanadia and titania in the V-TiO₂ composite through adsorption and photocatalysis of MB. MB was selected as a model reaction because it is widely used for dyeing in many industries such as paper, ink and used as cotton mordant with tannin [2].

Materials and Methods

Materials

The materials used for this study include titanium tetraisopropoxide (TTIP; 97%, Aldrich), absolute ethanol (99.98%, HmBG), acetylacetone ($\geq 99\%$, Aldrich), and vanadyl acetylacetonate (98%, Aldrich).

Synthesis of vanadia modified titania

Vanadia-modified titania (V-TiO₂) materials were prepared through the sol-gel method. The experimental procedures were reported in previous studies [2, 17]. In a typical synthesis, titanium tetraisopropoxide (TTIP; 97%, Aldrich) was mixed with absolute ethanol (99.98%, HmBG) and acetylacetone ($\geq 99\%$, Aldrich) according to the molar ratio of 1:100:2. The mixture was then stirred for 60 min at room temperature. Vanadia precursor was prepared separately by dissolving a pre-calculated amount of vanadyl acetylacetonate (98%, Aldrich) in acetylacetone. The two solutions were mixed and stirred for 30 minutes at room temperature, followed by evaporation at 353 K. The obtained solid material was calcined at 773 K for 5 hours. The molar ratio of vanadia in TiO₂ was varied from 1 to 10 mol%. The resulted materials were denoted as xV-TiO₂, where x represents mol% of V. Undoped TiO₂ was prepared with the same procedures without the addition of vanadyl acetylacetonate for comparison. Bulk V₂O₅ was prepared by evaporating vanadyl acetylacetonate (98%, Aldrich) in acetylacetone at 273 K, followed by calcination at 773 K for 5 hours.

Characterisation

Phase purity and crystallinity of the synthesised undoped TiO₂, vanadium oxide-modified titania, and bulk V₂O₅ samples were examined using Powder X-ray diffraction (XRD) analyser. The XRD measurements were conducted on Bruker Advance D8 X-ray diffractometer with Cu K α radiation ($\lambda = 0.15418$ nm, 40 KV, 40 mA, scan rate 0.1°/s). The Diffuse reflectance UV-visible (DR UV-Vis) spectra were recorded on Perkin Elmer Ultraviolet-visible Spectrometer Lambda 900 with BaSO₄ as reference. Bandgap energy of the samples was calculated from the extrapolation of the Tauc plot. Surface morphology of the prepared samples was investigated using Field Emission Scanning Electron Microscopy (FESEM). The samples were

coated with platinum using Auto Fine Coater (JEOL JFC-1600), prior to analysis using a FESEM instrument (JSM-6701F). The surface area and pore size distribution of the samples were confirmed using Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) equations from adsorption-desorption isotherms at 77 K obtained by using 3Flex Surface Characterisation Analyser (Micromeritics). Before analysis all the samples were degassed at 573 K for 4 hours. Temperature programmed reduction (TPR) was conducted to investigate the reducible species of surface vanadia on TiO₂. Selected samples were analysed in the temperature range of 573–973 K on Micromeritics AutoChem II chemisorption analyser. Prior to measurement, the samples were pre-treated under N₂ gas flowing at 473 K for 15 minutes. Argon gas, which contained 5.1% H₂, was passed through the sample tube during measurement with the flow rate of 25 cm³/min. Zeta potential of the samples was recorded on Malvern Zetasizer Nano ZSP.

Adsorption and photocatalytic degradation

Adsorption and photocatalytic testing were carried out on the synthesised materials. Aqueous solution of 50 mL 100 ppm MB solution and 0.1 g of the prepared material were placed in a beaker. Adsorption test was conducted prior to photocatalytic evaluation. The mixture was stirred in the dark at a constant temperature for 24 hours for the determination of adsorption capacity. Aliquots of 2 mL were withdrawn at different times within 24 hours and were put through a syringe filter. For the photocatalytic activity evaluation, the sample and MB solution were irradiated by a halogen fibre optic light illuminator (Dolan-Jenner MI 157, 150 W) as the visible light source for 24 hours straight after the adsorption test of 24 hours. A UV cut-off filter (400 nm, Edmund Optics) was used to filter the UV light. The photocatalytic activity of the samples was assessed using UV-Vis spectrophotometer (Thermo Fisher, Genesys 10S) to measure the concentration of MB solution before and after the photodegradation. Adsorption and photocatalytic activities of undoped TiO₂ and bulk V₂O₅ were also included for comparison.

Results and Discussion

Phases formation

As evidenced by XRD analysis (Figure 1), the undoped TiO₂ was in pure anatase phase, as its XRD pattern was well-matched with that reported in JCPDS 21-1272. The anatase phase remained after doping of 1 mol% V in 1V-TiO₂, but the peak becomes slightly broader. The crystallite sizes of the samples were calculated using the Scherrer equation, and the results are shown in Table 1. The crystallite size decreased with an increasing amount of V oxide modifier, suggesting the addition V oxide inhibited the crystal growth of TiO₂. As observed, the rutile phase was detected when 2 mol% and above of V oxide was added into TiO₂, indicating presence of an adequate amount of V has induced transformation of anatase to rutile phase. It was documented that due to the similar ionic radii of V⁴⁺ (0.580 Å) and V⁵⁺ (0.540 Å) to that of Ti⁴⁺ (0.605 Å) [18], making substitution of Ti by V at substitutional position possible. Therefore, it resulted in rutile phase formation [19]. The result was in good agreement with the previous study, which stated that the formation of the rutile phase upon V doping [20]. The detection of rutile phase was a good indication of successful V incorporated in the TiO₂ lattice, even though peaks assigned to V oxides were not detected in all the V-doped TiO₂ samples.

The undetectable V peaks could be attributed to a little amount of the V dopant (at low concentration of V dopant), or the dopant was highly dispersed on the TiO₂ surface. Alternatively, the undetectable vanadia peak was ascribed to amorphous nature of vanadia [21]. XRD pattern of the bulk V₂O₅ was in agreement with the reported pattern (JCPDS 01-0359), indicating it crystallised in orthorhombic structure. The current study indicated that the vanadium oxide present in the current sample was crystalline, not amorphous.

The percentage of anatase phase in the synthesized V-doped TiO₂ samples was calculated using the Spurr equation [22]:

$$A (\%) = 100 / (1 + 1.265 I_R / I_A) \quad (1)$$

where I_R is intensity of rutile peak at 2θ = 27.5° (110) and I_A is intensity of anatase peak at 2θ = 25.5° (101).

The percentage of rutile phase was obtained via subtraction of 100% on the calculated anatase percentage, assuming that the materials were totally crystallised.

Table 1 lists the anatase and rutile percentages in the synthesised samples. It was found that the percentage of rutile phase was independent to the amount of V dopant and remained constant in the range of 20.0% to 23.6%. The anatase to rutile transformation can be explained in terms of the valency state of the ion. Every four doping of V⁵⁺ in the Ti⁴⁺ octahedral cationic site led to one Ti⁴⁺ cation vacancy, which promotes the rutile phase formation. However, as the V amount increased, the accommodation of excess cation vacancy seems unfavourable in the anatase structure [23]. Hence, further addition of V oxide modifier did not promote more anatase-rutile transformation.

Optical properties

The prepared TiO₂ was a white powdered material, while the bulk V₂O₅ was an orange powder. All the V-TiO₂ samples were brownish. The colour of the V-TiO₂ samples was more intense, with the increase of the V content. A similar observation was reported previously [15]. As depicted in Figure 2, the undoped TiO₂ has absorption bands in the UV region ranged from 200-400 nm. The dominant peak found at 330 nm was identified as octahedral Ti species, while the shoulder at 230 nm was associated with tetrahedral coordinated Ti species [24]. Redshifts and new peaks of absorption within a range of 400-800 nm was observed after the modification with V oxides. In the resulting products, the extension in the absorption spectrum was demonstrated by the colour changes. The tailing of absorption curves revealed that all the V-TiO₂ materials absorbed the photon energy in the visible light region ranged 380-780 nm. The broadened peaks at 570 and 770 nm were due to V⁵⁺ and V⁴⁺, respectively [25]. As can be seen, the intensity of the V⁵⁺ absorption peak increased with the increase of V content in the samples. The 10V-TiO₂ sample possessed the highest amount of V⁵⁺, followed by 4V-TiO₂, 3V-TiO₂, 2V-TiO₂, and 1V-TiO₂. For bulk V₂O₅, the presence of a shoulder at 242 nm and two peaks at 380 and 480 nm were due to transitions in ligand-metal charge transfer (LMCT)

involving the charge transfer from oxygen ligands to the V^{5+} metal cation [26].

The bandgap energy of the samples was calculated from the Tauc plot. The following equation was used: $\alpha hv = A(hv - E_g)^{n/2}$, where α , hv , A , E_g are absorption coefficient, photon energy, a constant, and an optical bandgap, respectively. In this equation, n is determined by the transition type; n value is 1 and 4, for direct and indirect bandgap transitions. The value of α and E_g were first determined by plotting the graph $\ln(\alpha hv)$ vs. $\ln(hv - E_g)$, using an appropriate value of E_g . The value of n was determined from the slope of the straight line near the band edge. After that, $(\alpha hv)^{2/n}$ vs. hv was formed, and a tangential line was plotted along the band edge, with the tangent line x -intercept corresponding to the optical bandgap. The obtained results are tabulated in Table 1. The findings showed that the bandgap energy of TiO_2 (3.25 eV) dropped significantly after doping of 1 mol% V into TiO_2 (2.15 eV). The bandgap energy of TiO_2 was further decreased with increasing of V amount. It was believed that the 3d orbital of vanadia had reduced the bandgap energy of TiO_2 . The lowest bandgap energy of 1.50 eV was achieved in 10V- TiO_2 .

Morphology

FESEM images of undoped TiO_2 and selected V- TiO_2 samples are illustrated in Figure 3. Undoped TiO_2 (Figure 3(a)) appeared to be large blocks of coarse material. The addition of 1 mol% V dopant also displayed similar features to undoped TiO_2 , but with the formation of more small particles on the large material. Also, holes are formed between the particles, as shown in Figure 3(b).

Sample 4V- TiO_2 showed more small particles agglomerated with reduced holes between the small particles on the surface of the larger particle course. The surface of 10V- TiO_2 sample was smoother and more homogeneous, with small spherical particles agglomerated on the surface of TiO_2 . The current results revealed that the addition of V oxide modifier could alter the morphology of undoped TiO_2 powder to be smoother. The FESEM images of V- TiO_2 supported the XRD results whereby the addition of excess V dopants (> 2 mol%) was not favourable in the anatase structure

and could have resided on the surface of TiO_2 to form V_2O_5 .

Textural analysis

The nitrogen adsorption-desorption isotherms of samples are presented in Figure 4. All synthesised samples possessed type IV isotherm, which is the characteristic of a mesoporous material. From the isotherm curve, it was observed that undoped TiO_2 , 1V- TiO_2 , and 2V- TiO_2 have H3 hysteresis loops, indicating the samples have slit-shaped pores. As the amount of V dopant increased, the hysteresis loops changed from H3 to H2 for samples 3V- TiO_2 and 4V- TiO_2 , indicating these samples have bottleneck shape pore. Meanwhile, 10V- TiO_2 has hysteresis loop of H1, denoting the pore shape was cylinder-shaped. It was observed that the closing of the hysteresis loop of samples 1 to 4 mol% V- TiO_2 was approximately at 0.45 P/P₀, while the closing loop of 10V- TiO_2 was at 0.75 P/P₀. The results suggested that former samples had smaller mesopores while the latter sample had larger mesopores. In addition, 10V- TiO_2 possessed macropores since it showed a slight increase in adsorption in 0.95–1.00 P/P₀.

The specific surface area, total pore volume, and average pore diameter of samples are tabulated in Table 2. Increasing amount of V oxide modifier increased the surface area of TiO_2 by 2-fold from 7 to 34 $m^2 g^{-1}$. The increase of the surface area could be ascribed to the presence of V, which inhibited the crystalline growth, leading to an enlarged surface area. However, the addition of 10 mol% V reduced the surface area to 23 $m^2 g^{-1}$. This was due to the excess modifier covering the surface of TiO_2 , as demonstrated by Figure 3(d). It is evident from Figure 3(d) that the surface of 10V- TiO_2 had been covered up by the modifier compared to Figure 3(a), which depicts the TiO_2 without a modifier.

Addition of 1 to 3 mol% V has a negligible effect on the total pore volume. The increase of pore volume of 4V- TiO_2 and 10V- TiO_2 samples was in agreement with the changing of the hysteresis loop, whereby the hysteresis loop H2 of 4V- TiO_2 was larger as compared to 3V- TiO_2 sample. Meanwhile, 10V- TiO_2 has the most significant total pore volume among the samples because it

possessed macropores as evidenced by the isotherm plot.

The BJH pore size distribution is shown in Figure 5. The pore size was tuneable with the addition of V oxide modifier. The pore size distribution of samples with less than 4 mol% V became more homogenous and shifted to smaller pore size.

The current result is supported by the FESEM images where the pores between particles (textural) were reduced. The average pore diameter of 10V-TiO₂ was the largest among the samples. Figure 5 shows that 10V-TiO₂ has pores larger than 50 nm, confirming that this sample consisted of a mixture of meso and macropores, leading to the largest average pore diameter.

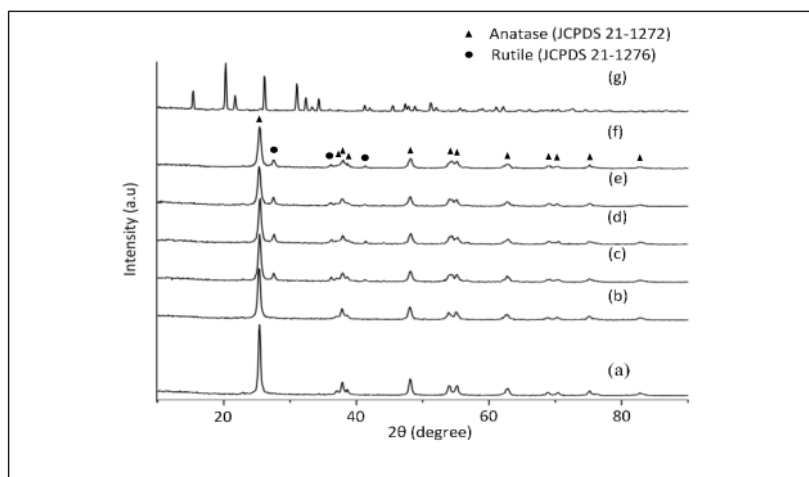
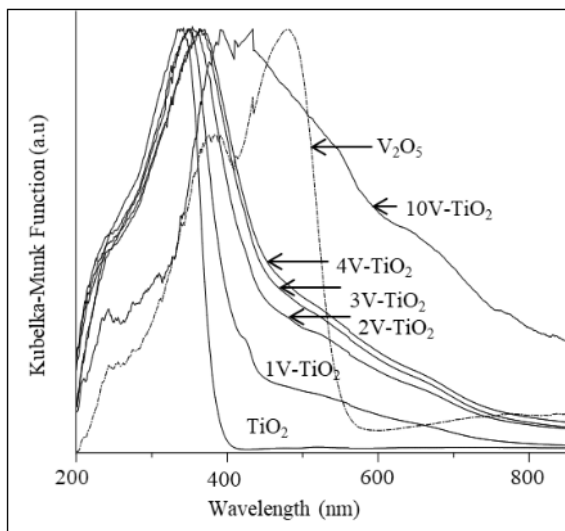


Figure 1. XRD patterns of (a) TiO₂, (b) 1V-TiO₂, (c) 2V-TiO₂, (d) 3V-TiO₂, (e) 4V-TiO₂, (f) 10V-TiO₂, and (g) V₂O₅

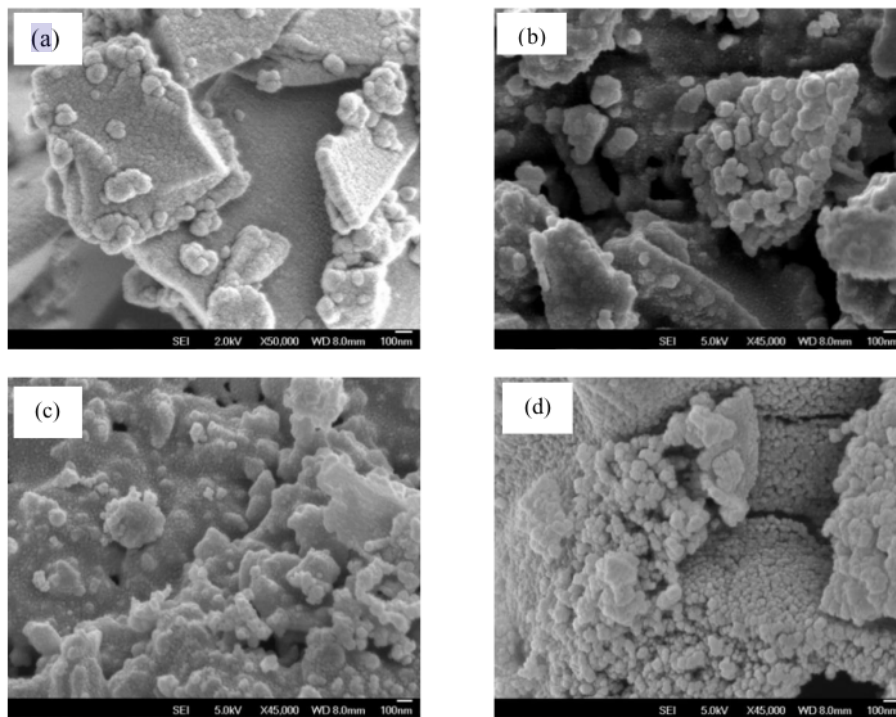
Table 1. Phases composition, crystallite size and bandgap energy of TiO₂, V₂O₅ and V-TiO₂ samples 73

Sample	Anatase (%) ^a	Rutile (%) ^b	Crystallite size (nm)	Bandgap (eV) ^c
TiO ₂	100.0	n.a.	20.1	3.25
1V-TiO ₂	100.0	n.a.	16.2	2.75
2V-TiO ₂	80.0	20.0	16.5	2.00
3V-TiO ₂	77.4	22.6	14.7	1.95
4V-TiO ₂	76.4	23.6	14.8	1.80
10V-TiO ₂	78.2	21.8	14.5	1.50
V ₂ O ₅	n.a	n.a	n.a	2.30

^a Calculated from Spurr equation, ^b Calculated from 100%- anatase phase%, ^c Calculated from extrapolation of Tauc plot and n.a. – not available



11
Figure 2. DR-UV-Vis spectra of TiO_2 , V_2O_5 , and V-doped TiO_2 samples



5
Figure 3. FESEM images of (a) TiO_2 (magnification $\times 50,000$), (b) 1V- TiO_2 (magnification $\times 45,000$), (c) 4V- TiO_2 (magnification $\times 45,000$), and (d) 10V- TiO_2 (magnification $\times 45,000$)

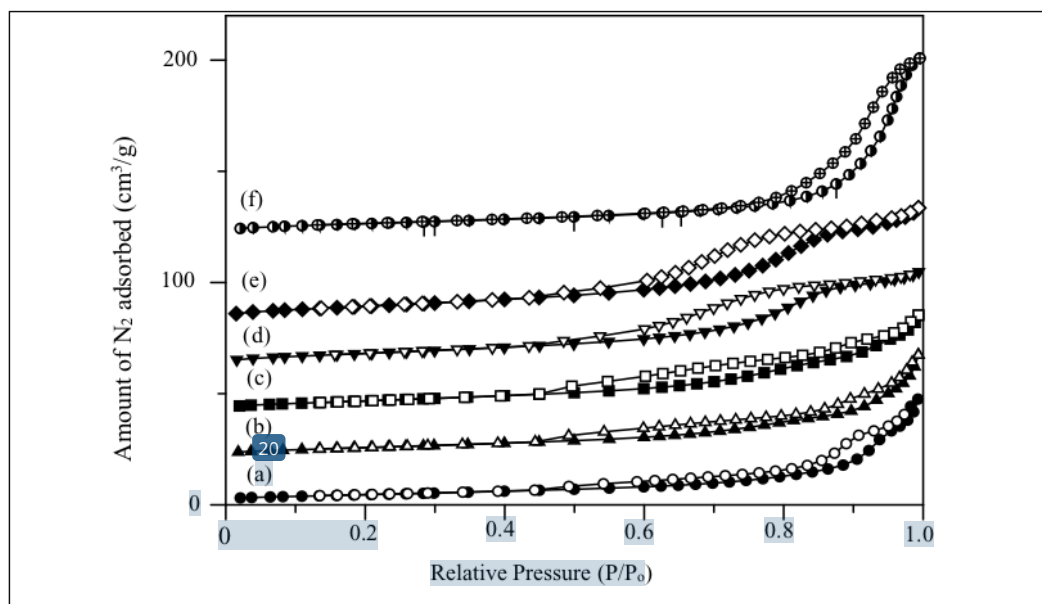


Figure 4. N_2 adsorption-desorption isotherms of (a) TiO_2 , (b) 1V- TiO_2 , (c) 2V- TiO_2 , (d) 3V- TiO_2 , (e) 4V- TiO_2 , and (f) 10V- TiO_2 . (Remarks: filled points are adsorption isotherms, empty points are desorption isotherms. Figures (b)–(f) are marginally moved upwards for 20, 40, 60, 80, and 120 cm^3/g , respectively for clearer presentation).

Table 2. Surface area, total pore volume and average pore diameter of TiO_2 and V- TiO_2 samples

Sample	Surface Area ($m^2 g^{-1}$)	Total Pore Volume ($cm^3 g^{-1}$)	Average Pore Diameter (\AA)
TiO_2	17	0.0677	164.27
1V- TiO_2	21	0.0659	125.94
2V- TiO_2	25	0.0649	105.38
3V- TiO_2	29	0.0660	90.12
4V- TiO_2	34	0.0794	94.78
10V- TiO_2	23	0.1218	212.00

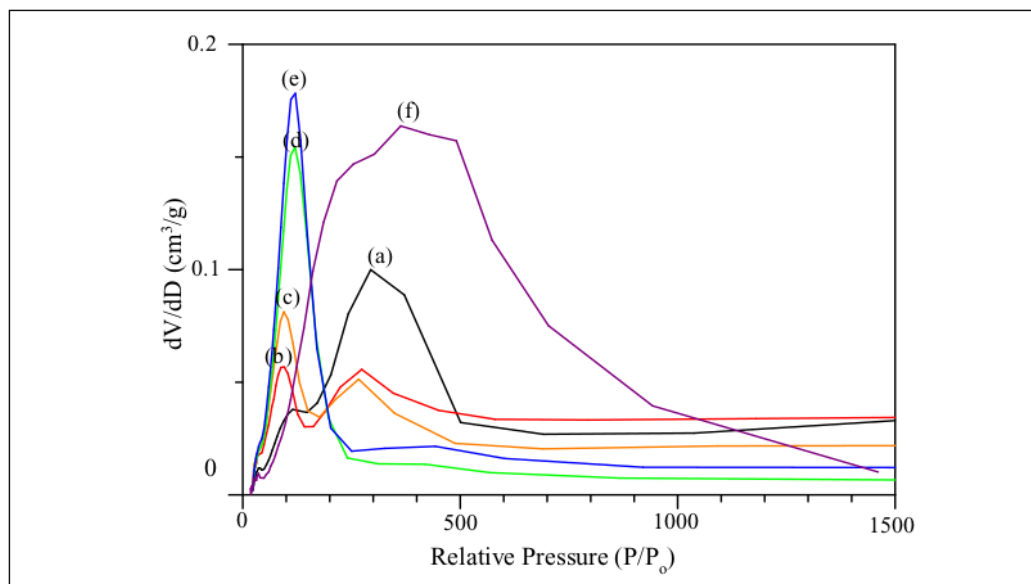


Figure 5. BJH pore size distributions of (a) TiO₂, (b) 1V-TiO₂, (c) 2V-TiO₂, (d) 3V-TiO₂, (e) 4V-TiO₂, and (f) 10V-TiO₂

Surface oxidation state analysis

Temperature program reduction (TPR) was performed on selected samples to analyse vanadium surface oxidation states in the samples. H₂-TPR spectra of V-TiO₂ samples and V₂O₅ are shown in Figure 6. The 1 mol% V gave only one reduction peak at 814.3 K, which corresponded to the reduction of V₆O₁₃ to V₂O₄ [27], indicating that V⁴⁺ existed dominantly in 1V-TiO₂. The higher amount of V oxide modifier (4 mol%) resulted in a lower reduction peak at 647.4 K in 4V-TiO₂. This peak was associated with the reduction of V₂O₅ to V₆O₁₃ [27]; hence, it was a good indication of V⁵⁺ species existence. The detection of this peak is always linked to the formation of the strong interaction between V species and the H₂ gas due to V-O-Ti bonds of higher reducibility. Besides, a hump at 765.1 K was also observed in 4V-TiO₂, implying the presence of trace V⁴⁺ species.

Similarly, 10V-TiO₂ exhibited two reduction peaks at 684.5 and 841.3 K. Figure 6 shows that the intensity of the reduction peak at 684.5 K is remarkably higher than that of 4V-TiO₂, strongly indicating the existence of more V⁵⁺ in 10V-TiO₂ compared to the latter sample. The maximum reduction temperature and the corresponded hydrogen consumption of each sample are tabulated in Table 3. As observed, the amount of V⁵⁺ in the 10V-TiO₂ was 5-fold of that in 4V-TiO₂. The bulk V₂O₅ showed only one reduction peak at 867.6 K, which corresponded to bulk vanadate. It was reported that more bulk vanadate was formed with increasing of vanadia content in vanadia-titania catalyst [27].

The contradiction could be due to different synthetic method and calcination temperature applied in the studies. The authors had synthesised vanadia-titania via the impregnation method at 673 K. Unlike the impregnation method, the sol-gel method applied in the current work was believed to enable the loading of vanadia not only on the TiO₂'s surface but also in the

TiO₂ lattice. Meanwhile, the higher calcination temperature of 773 K had resulted in more interaction between vanadia and TiO₂ that facilitated the formation of more reducible V⁵⁺ species in the materials [28]. In the present work, the decrease of reduction temperature in V₂O₅ in the presence of TiO₂ can be explained by the structure distortion in V₂O₅ due to the extensive interaction with the TiO₂ support. A similar phenomenon was found for 12-molybdophosphoric acid supported on V₂O₅ dispersed γ -Al₂O₃ catalyst [29]. Therefore, we conclude that the presence of TiO₂ phase is essential as support for V⁵⁺ species formation.

Adsorption and photocatalytic performance

Adsorption and photocatalytic activity of the resulting V-TiO₂ samples were assessed over decolourisation of MB. As illustrated in Figure 7, the adsorption of MB on undoped TiO₂ is only 3% after 24 hours. Doping of 1 mol% V into TiO₂ allows 1V-TiO₂ to adsorb 9% MB after 2 hours. The increased V dopant amount of 2, 3, 4, and 10 mol% V had further enhanced the MB adsorption to 18%, 25%, 31%, and 68% after 2 hours. The adsorption of MB increased significantly by the increasing amount of V in V-TiO₂. The results demonstrated that the adsorption capacity of 10V-TiO₂ was 26-folds higher than that of undoped TiO₂. This material adsorbed 95% MB after 24 hours, confirming it was an excellent adsorbent for MB.

Zeta potential was conducted to analyse the surface charge of the samples. It was found that the increased amount of V oxide modifier to 10 mol% decreases the isoelectric point (IEP) continuously from 4.23 to 2.01 (Table 3). This could be the reason for the tremendous increase of MB adsorption, a cationic dye, up to 68% after 2 hours when TiO₂ was modified with 10 mol% V oxide. In addition, MB has a high affinity for V⁵⁺ [30]. This further enhanced the adsorption capacity of MB on 10V-TiO₂, which possessed the highest amount of V⁵⁺ among the samples. Comparatively, the adsorption ability of the bulk V₂O₅ was poorer as it adsorbed only 40% of MB after 2 hours. The lower activity of bulk V₂O₅ could be attributed to its massive structure which makes the accessibility of MB on V⁵⁺ more difficult. Besides, the superior adsorption capability of 10V-TiO₂ as compared to bulk V₂O₅ could be due to the existence

of more surface OH⁻ in 10V-TiO₂ to interact with the π -electron of MB [16, 31].

The photocatalytic activity evaluation was carried out straight after the adsorption test with the samples. Figure 7 displays that the undoped TiO₂ gave an activity of 14.4% of MB photodegradation even with the utilisation of UV cut-off filter (400 nm, Edmund Optics). This can be rationalised by the photosensitisation effect [32]. Usage of MB as a model reaction in photocatalysis has been highlighted by Ohtani and co-worker [33]. The authors claimed that MB was not an acceptable pollutant for the target study, particularly when it was degraded under visible light. However, Matos et al. [34] argued that the decolourisation of MB is suitable for assessing the photocatalytic behaviour of semiconductors under steady-state conditions of the effect of photon flux upon the first-order rate constant.

Among the V-TiO₂ samples, only the 4V-TiO₂ sample has photodegraded 13.5% of MB after 24 hours under visible light irradiation. The other V-TiO₂ samples have negligible photocatalytic activity under visible light irradiation. In contrast, it had been documented that photocatalytic activity TiO₂ in dye degradation was significantly enhanced after V doping [35]. The photocatalytic improvement was always associated with the extended optical absorption of TiO₂ to the visible light, reduction in bandgap energy and the presence of anatase/rutile mixing phase. In the present study, the MB molecules were preferably adsorbed at the V site due to the high affinity of V⁵⁺. The strong interaction between V⁵⁺ and the MB molecules was believed to hinder the diffusion of the dye molecules to the active site for photodegradation at Ti; hence, retard the photocatalytic activity of the V-doped TiO₂ samples. In 4V-TiO₂, only limited MB molecules that adsorbed at Ti site would be further photodegraded after irradiated under visible light. The schematic diagram showing roles of the vanadia and titania phases in the dye removal is illustrated in Figure 8.

Even though the photocatalytic activity of the V-TiO₂ was not comparable to its adsorption ability, the total removal of MB of V-TiO₂ significantly increased as compared to TiO₂ and V₂O₅. As mentioned, the

photo³³lytic enhancement of TiO₂ was always related to the extension of optical absorption to the visible light region. By comparing the adsorption and photocatalytic testing of V-TiO₂ sample³⁴ the XRD results as represented in Figure 1 and Table 1, it can be seen that part of the anatase to rutile phase transformation induced by the doping of V into TiO₂ might have enhanced the photodegradation of MB to visible¹⁵ light region, attributed by the¹⁵ lower bandgap energy (3.0 eV) of the rutile phase as compared to the anatase phase (3.2 eV).¹⁵ suggested in this study that the vanadia and titania played a different role in the ad⁶²sorption-photocatalytic activity. The vanadia responsible for the anatase to ru⁴⁹ phase transformation as well as the shifting of the absorption properties of TiO₂ to visible light region, and at the same time, acted as an adsorbent, while the titania acted as the photocatalyst, responsible for the photodegradation activity.

Reusability test

Since 10V-TiO₂ has the highest removal of MB, it was³⁷ sen for the reusability test. The used 10V-TiO₂ was washed with distilled water several times and dried at

333 K. The reusability test was conducted for four successive¹⁷ cles under the same conditions. It was found out that the adsorption capacity of the used-10V-TiO₂ decreased significantly to 28%, 26%, and 27% for second, third, and fourth cycles, respectively. The decrease of the adsorption capacity could be attributed to the leaching problem of vanadium oxide from the material. It was believed that the loss of the vanadium oxide could have decreased the hydroxyl surface group and hence leading to less adsorption of MB [36]. It was noted that after the adsorption for the first cycle, the adsorption for the rest of the cycles was almos⁴³nstant, indicating that the material has become stable. It is worth to highlight that the photocatalytic performance of 10V-TiO₂ increased to approximately 30% for the second, third, and fourth cycles (Figure 9). The improvement in photocatalytic performance could be attributed to more TiO₂ were exposed to MB, leading to a more significant degradation of MB. The study indicated that 10V-TiO₂ was a good photocatalyst for MB photodegradation after second cycles onwards.

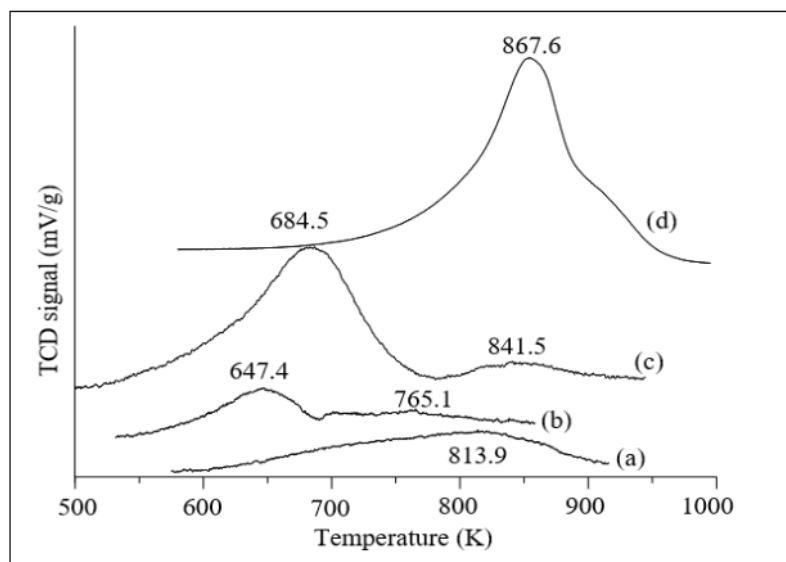


Figure 6. TPR profiles of (a) 1V-TiO₂, (b) 4V-TiO₂, (c) 10V-TiO₂, (d) V₂O₅ (Intensity of V₂O₅ is multiplied with 0.1)

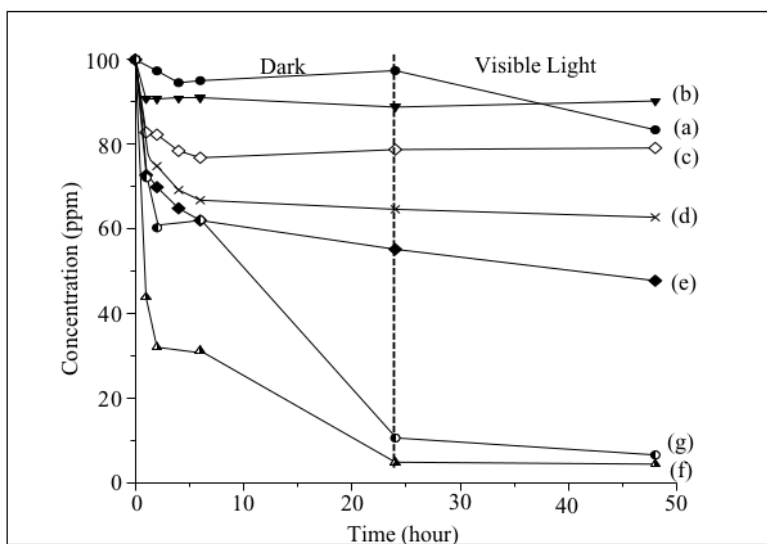


Figure 7. The adsorption and photodegradation of MB using (a) TiO₂, (b) 1V-TiO₂, (c) 2V-TiO₂, (d) 3V-TiO₂, (e) 4V-TiO₂, (f) 10V-TiO₂, (g) V₂O₅

Table 3. Isoelectric point of prepared samples and its corresponded adsorption efficiency after 2 hours

Entry	Sample	IEP/pH	Adsorption Efficiency After 2 hours /%
1	TiO ₂	4.23	3
2	1V-TiO ₂	4.14	9
3	2V-TiO ₂	4.13	18
4	3V-TiO ₂	4.12	25
5	4V-TiO ₂	2.22	31
6	10V-TiO ₂	2.01	68

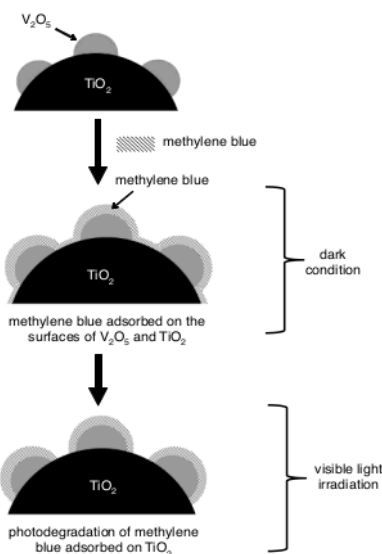


Figure 8. Schematic diagram showing the roles of vanadia and titania

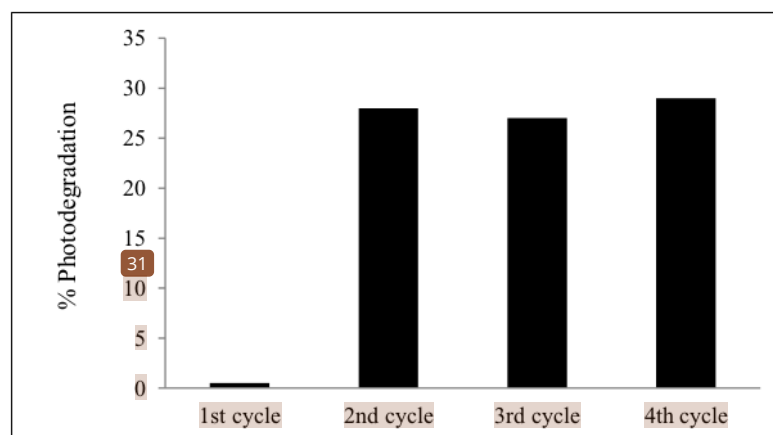


Figure 9. Reusability test of 10V-TiO₂. (Conditions: concentration of MB = 100 ppm, mass of sample used = 0.1 g)

Conclusion

A series of V modified TiO₂ was successfully synthesised via the sol-gel method. Roles of vanadia and titania phases in the removal of MB were examined. The results demonstrated that the presence of vanadia phase was responsible for the rutile phase generation, bandgap

reduction, and wavelength extension in the V-TiO₂ samples. On the other hand, the titania phase played a crucial role as support for the formation of more V⁵⁺ species. In the V oxide modified TiO₂ materials, vanadia phase was an excellent adsorbent attributed to the presence of V⁵⁺ species is abundant, which has a high

affinity towards MB. Meanwhile, the titania phase acted as the photocatalyst in degrading MB. 10V-TiO₂ showed high photostability and reusability in photodegrading MB in second cycles and onward, attributed to more exposed of TiO₂ to MB.

Acknowledgement

Authors are grateful to financial support from Ministry of Higher Education Malaysia (MOHE) and Universiti Teknologi Malaysia through UTM Transdisciplinary Research Grant (Cost Centre No. Q.J130000.3554.07G57) and Professional Development Research University (Cost Centre No. Q.J.130000.21A2.03E61).

References

- Koh, P. W., Yuliati, L. and Lee, S. L. (2019). Kinetics and optimization studies of photocatalytic degradation of methylene blue over Cr-doped TiO₂ using response surface methodology. *Iranian Journal of Science and Technology, Transactions A: Science*, 43(1): 95-103.
- Koh, P. W., Hatta, M. H. M., Ong, S. T., Yuliati, L. and Lee, S. L. (2017). Photocatalytic degradation of photosensitizing and non-photosensitizing dyes over chromium doped titania photocatalysts under visible light. *Journal of Photochemistry and Photobiology A: Chemistry*, 332: 215-223.
- Kumar, P. S., Ramalingam, S. and Sathishkumar, K. (2011). Removal of methylene blue dye from aqueous solution by activated carbon prepared from cashew nut shell as a new low-cost adsorbent. *Korean Journal of Chemical Engineering*, 28(1): 149-155.
- Roosta, M., Ghaedi, M., Daneshfar, A., Sahraei, R. and Asghari, A. (2014). Optimization of the ultrasonic assisted removal of methylene blue by gold nanoparticles loaded on activated carbon using experimental design methodology. *Ultrasonics Sonochemistry*, 21(1): 242-252.
- Keng, P. S., Lee, S. L., Ha, S. T., Hung, Y. T. and Ong, S. T. (2013). Cheap materials to clean heavy metal polluted waters. In *Green Materials for Energy, Products and Depollution* Springer, Dordrecht: pp. 335-414.
- Leong, C. Y., Koh, P. W., Lo, Y. S., Lee, S. L. (2020). Hydrothermal synthesis of titanium dioxide nanotube with methylamine for photodegradation of Congo red. *IOP Conf. Series: Materials Science and Engineering*, 833, 012075.
- Pirkanniemi, K. and Sillanpää, M. (2002). Heterogeneous water phase catalysis as an environmental application: a review. *Chemosphere*, 48(10): 1047-1060.
- MiarAlipour, S., Friedmann, D., Scott, J. and Amal, R. (2018). TiO₂/porous adsorbents: Recent advances and novel applications. *Journal of Hazardous Materials*, 341: 404-423.
- Ooi, Y. K., Hussin, F., Yuliati, L. and Lee, S. L. (2019). Comparison study on molybdena-titania supported on TUD-1 and TUD-C synthesized via sol-gel templating method: Properties and catalytic performance in olefins epoxidation. *Materials Research Express*, 6(7): 074001.
- Ooi, Y. K., Yuliati, L., Hartanto, D., Nur, H. and Lee, S. L. (2016). Mesoporous TUD-C supported molybdena doped titania as high selective oxidative catalyst for olefins epoxidation at ambient condition. *Microporous and Mesoporous Materials*, 225: 411-420.
- Wang, N., Zhu, L. H., Li, J., and Tang, H. Q. (2007). A novel Fe(OH)₃/TiO₂ nanoparticles and its high photocatalytic activity. *Chinese Chemical Letters*, 18(10): 1261-1264.
- Hamdan, H., Muhid, M. N. M., Lee, S. L., and Tan, Y. Y. (2009). Visible light enabled V and Cr doped titania-silica aerogel photocatalyst. *International Journal of Chemical Reactor Engineering*, 7(1).
- Ooi, Y. K., Yuliati, L., and Lee, S. L. (2016). Phenol photocatalytic degradation over mesoporous TUD-1-supported chromium oxide-doped titania photocatalyst. *Chinese Journal of Catalysis*, 37(11): 1871-1881.
- Wu, J. C. S. and Chen, C. H. (2004). A visible-light response vanadium-doped titania nanocatalyst by sol-gel method. *Journal of Photochemistry and Photobiology A: Chemistry*, 163(3): 509-515.

15. Li, H., Zhao, G., Chen, Z., Han, G. and Song, B. (2010). Low temperature synthesis of visible light-driven vanadium doped titania photocatalyst. *Journal of Colloid and Interface Science*, 344(2): 247-250.
16. Nguyen, T. B., Hwang, M. J., and Ryu, K. S. (2012). High adsorption capacity of V-doped TiO₂ for decolorization of methylene blue. *Applied Surface Science*, 258(19): 7299-7305.
17. Koh, P. W., Yuliati, L., and Lee, S. L. (2014). Effect of transition metal oxide doping (Cr, Co, V) in the photocatalytic activity of TiO₂ for congo red degradation under visible light. *Jurnal Teknologi (Sciences & Engineering)*, 69(5): 45-50.
18. Shannon, R. D. (1976). Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica Section A: Crystal Physics, Diffraction, Theoretical and General Crystallography*, 32(5): 751-767.
19. Choi, J., Park, H. and Hoffmann, M. R. (2009). Effects of single metal-ion doping on the visible-light photoreactivity of TiO₂. *The Journal of Physical Chemistry C*, 114(2): 783-792.
20. Martin, S. T., Morrison, C. L., and Hoffmann, M. R. (1994). Photochemical mechanism of size-quantized vanadium-doped TiO₂ particles. *The Journal of Physical Chemistry*, 98(51): 13695-13704.
21. Pena, D. A., Uphade, B. S., and Smirniotis, P. G. (2004). TiO₂-supported metal oxide catalysts for low-temperature selective catalytic reduction of NO with NH₃: I. Evaluation and characterization of first row transition metals. *Journal of Catalysis*, 221(2), 421-431.
22. Spurr, R. A. and Myers, H. (1957). Quantitative analysis of anatase-rutile mixtures with an X-ray diffractometer. *Analytical Chemistry*, 29(5): 760-762.
23. Nagaveni, K., Hegde, M. S. and Madras, G. (2004). Structure and photocatalytic activity of Ti_{1-x}M_xO_{2±δ} (M= W, V, Ce, Zr, Fe, and Cu) synthesized by solution combustion method. *The Journal of Physical Chemistry B*, 108(52): 20204-20212.
24. Astorino, E., John, B. Peri, R. J. Willey, and Guido B. (1995). Spectroscopic characterization of silicalite-1 and titanium silicalite-1. *Journal of Catalysis*, 157(2): 482-500.
25. Bhattacharyya, K., Varma, S., Tripathi, A. K., Bharadwaj, S. R., and Tyagi, A. K. (2008). Effect of vanadia doping and its oxidation state on the photocatalytic activity of TiO₂ for gas-phase oxidation of ethene. *The Journal of Physical Chemistry C*, 112(48): 19102-19112.
26. Lewandowska, A. E., Banares, M. A., Khabibulin, D. F. and Lapina, O. B. (2009). Precursor effect on the molecular structure, reactivity, and stability of alumina-supported vanadia. *The Journal of Physical Chemistry C*, 113(48): 20648-20656.
27. Shekar, S. C., Soni, K., Bunkar, R., Sharma, M., Singh, B., Suryanarayana, M. V. S., and Vijayaraghavan, R. (2011). Vapor phase catalytic degradation of bis (2-chloroethyl) ether on supported vanadia-titania catalyst. *Applied Catalysis B: Environmental*, 103(1-2): 11-20.
28. Olthof, B., Khodakov, A., Bell, A. T. and Iglesia, E. (2000). Effects of support composition and pretreatment conditions on the structure of vanadia dispersed on SiO₂, Al₂O₃, TiO₂, ZrO₂, and HfO₂. *The Journal of Physical Chemistry B*, 104(7): 1516-1528.
29. Rao, P. S. N., Rao, K. T. V., Prasad, P. S. S. and Lingaiah, N. (2011). The role of vanadia for the selective oxidation of benzyl alcohol over heteropolymolybdate supported on alumina. *Chinese Journal of Catalysis*, 32(11-12): 1719-1726.
30. Zhao, L., Zhu, X., Feng, K., and Wang, B. (2006). Speciation analysis of inorganic vanadium (V(IV)/V(V)) by graphite furnace atomic absorption spectrometry following ion-exchange separation. *International Journal of Environmental and Analytical Chemistry*, 86(12): 931-939.
31. Dong, Y., Liu, Y., Lu, D., Zheng, F., Fang, P. and Zhang, H. (2017). Unpredictable adsorption and visible light induced decolorization of nano rutile for the treatment of crystal violet. *Solid State Sciences*, 66: 1-6.

32. Yu, L., Yuan, S., Shi, L., Zhao, Y. and Fang, J. (2010). Synthesis of Cu²⁺ doped mesoporous titania and investigation of its photocatalytic ability under visible light. *Microporous and Mesoporous Materials*, 134(1-3): 108-114.
33. Yan, X., Ohno, T., Nishijima, K., Abe, R. and Ohtani, B. (2006). Is methylene blue an appropriate substrate for a photocatalytic activity test? A study with visible-light responsive titania. *Chemical Physics Letters*, 429(4-6): 606-610.
34. Matos, J., Hofman, M. and Pietrzak, R. (2013). Synergy effect in the photocatalytic degradation of methylene blue on a suspended mixture of TiO₂ and N-containing carbons. *Carbon*, 54: 460-471.
35. Nair, R. G., Roy, J. K., Samdarshi, S. K. and Mukherjee, A. K. (2012). Mixed phase V doped titania shows high photoactivity for disinfection of *Escherichia coli* and detoxification of phenol. *Solar Energy Materials and Solar Cells*, 105: 103-108.
36. Wu, H-X, Wang, T-J, Chen, L., Jin, Y., Zhang, Y. and Dou, X-M. (2009). The roles of the surface charge and hydroxyl group on a Fe-Al-Ce adsorbent in fluoride adsorption. *Industrial & Engineering Chemistry Research*, 48(9): 4530-4534.

20%

SIMILARITY INDEX

9%

INTERNET SOURCES

18%

PUBLICATIONS

4%

STUDENT PAPERS

PRIMARY SOURCES

- 1 P. W. Koh, L. Yuliaty, S. L. Lee. "Kinetics and Optimization Studies of Photocatalytic Degradation of Methylene Blue over Cr-Doped TiO₂ using Response Surface Methodology", Iranian Journal of Science and Technology, Transactions A: Science, 2017
Publication 2%
 - 2 Romissaa Saleh, Ayman H. Zaki, Fatma I. Abo El-Ela, Ahmed A. Farghali, Mohamed Taha, Rehab Mahmoud. "Consecutive removal of heavy metals and dyes by a fascinating method using titanate nanotubes", Journal of Environmental Chemical Engineering, 2021
Publication 1%
 - 3 K. Nagaveni, M. S. Hegde, Giridhar Madras. "Structure and Photocatalytic Activity of Ti M O (M = W, V, Ce, Zr, Fe, and Cu) Synthesized by Solution Combustion Method ", The Journal of Physical Chemistry B, 2004
Publication 1%
-

4

Thanh-Binh Nguyen, Moon-Jin Hwang, Kwang-Sun Ryu. "High adsorption capacity of V-doped TiO₂ for decolorization of methylene blue", Applied Surface Science, 2012

Publication

1 %

5

Suryakanta Nayak, Banalata Sahoo, Dipak Khastgir. " Flexible Nanocomposites Comprised of Poly(dimethylsiloxane) and High-Permittivity TiO Nanoparticles Doped with La /Cu for Dielectric Applications ", ACS Applied Nano Materials, 2019

Publication

1 %

6

Yee Khai Ooi, Faisal Hussin, Leny Yuliati, Siew Ling Lee. "Comparison study on molybdena-titania supported on TUD-1 and TUD-C synthesized via sol-gel templating method: Properties and catalytic performance in olefins epoxidation", Materials Research Express, 2019

Publication

1 %

7

Submitted to Indian Institute of Technology

Student Paper

1 %

8

Parisa Pourdayhimi, Pei Wen Koh, Hadi Nur, Siew Ling Lee. "Highly Crystalline Zinc Oxide/Mesoporous Hollow Silica Composites Synthesized at Low Temperature for the Photocatalytic Degradation of Sodium

<1 %

Dodecylbenzenesulfonate", Australian Journal of Chemistry, 2019

Publication

9

Zhang, S.. "Visible-light-driven photocatalyst of Bi₂WO₆ nanoparticles prepared via amorphous complex precursor and photocatalytic properties", Journal of Solid State Chemistry, 200601

Publication

<1 %

10

Ken-ichi KATSUMATA, Tetsuya SHICHI, Akira FUJISHIMA. "Photo-induced hydrophilicity of polycrystalline SrTiO₃ thin films", Journal of the Ceramic Society of Japan, 2010

Publication

<1 %

11

K. Bhattacharyya, S. Varma, A. K. Tripathi, S. R. Bharadwaj, A. K. Tyagi. " Effect of Vanadia Doping and Its Oxidation State on the Photocatalytic Activity of TiO for Gas-Phase Oxidation of Ethene ", The Journal of Physical Chemistry C, 2008

Publication

<1 %

12

Submitted to Universiti Malaysia Sarawak

Student Paper

<1 %

13

Romissaa Saleh, Ayman H. Zaki, Fatma I. Abo El-Ela, Ahmed A. Farghali, Mohamed Taha, Rehab K. Mahmoud. "Consecutive removal of heavy metals and dyes by a fascinating

<1 %

method using titanate nanotubes", Journal of Environmental Chemical Engineering, 2020

Publication

14

doras.dcu.ie

Internet Source

<1 %

15

Green Energy and Technology, 2011.

Publication

<1 %

16

Ken-ichi Katsumata, Ryosuke Motoyoshi, Nobuhiro Matsushita, Kiyoshi Okada.

"Preparation of graphitic carbon nitride (g-C₃N₄)/WO₃ composites and enhanced visible-light-driven photodegradation of acetaldehyde gas", Journal of Hazardous Materials, 2013

Publication

<1 %

17

[repository.futminna.edu.ng:8080](https://repository.futminna.edu.ng/8080)

Internet Source

<1 %

18

dr.ntu.edu.sg

Internet Source

<1 %

19

Submitted to Coventry University

Student Paper

<1 %

20

ujcontent.uj.ac.za

Internet Source

<1 %

21

Juan Matos, Ricmary Montaña, Elicam Rivero.

"Influence of activated carbon upon the photocatalytic degradation of methylene blue

<1 %

under UV-vis irradiation", Environmental Science and Pollution Research, 2014

Publication

22

Jung-Hoon Yu, Sang-Hun Nam, Ji Won Lee, Dong In Kim, Jin-Hyo Boo. "Oxidation state and structural studies of vanadium-doped titania particles for the visible light-driven photocatalytic activity", Applied Surface Science, 2018

Publication

23

Khushboo Srivastava, Vijay Devra, Ashu Rani. "Fly ash supported vanadia catalyst: An efficient catalyst for vapor phase partial oxidation of toluene in a micro-reactor", Fuel Processing Technology, 2014

Publication

24

Pourkhalil, Mahnaz, Abdolsamad Zarringhalam Moghaddam, Alimorad Rashidi, Jafar Towfighi, and Yadollah Mortazavi. "Preparation of highly active manganese oxides supported on functionalized MWNTs for low temperature NO_x reduction with NH₃", Applied Surface Science, 2013.

Publication

25

bmcchem.biomedcentral.com

Internet Source

26

Tong, T.. "Preparation of Fe³⁺-doped TiO₂ catalysts by controlled hydrolysis of titanium

<1 %

<1 %

<1 %

<1 %

<1 %

alkoxide and study on their photocatalytic activity for methyl orange degradation", Journal of Hazardous Materials, 20080715

Publication

27

research-repository.griffith.edu.au

Internet Source

<1 %

28

Alam S.M. Nur, Marzia Sultana, Atol Mondal, Sumon Islam, Fataha Nur Robel, Aminul Islam, Mst. Sumaia Aktar Sumi. "A review on the development of elemental and codoped TiO₂ photocatalysts for enhanced dye degradation under UV-vis irradiation", Journal of Water Process Engineering, 2022

Publication

<1 %

29

Hao Zhou, MengYao Ge, Shiguo Wu, Bichao Ye, Yaxin Su. "Iron based monolithic catalysts supported on Al₂O₃, SiO₂, and TiO₂: A comparison for NO reduction with propane", Fuel, 2018

Publication

<1 %

30

Xiao, W.. "TiN film with (111) preferred orientation as a visible-light-driven photocatalyst for hydrogen evolution from water decomposition", Materials Chemistry & Physics, 20070915

Publication

<1 %

31

scholarworks.uaeu.ac.ae

Internet Source

<1 %

32

Hayat Khan, Dimitrios Berk. "Synthesis, physicochemical properties and visible light photocatalytic studies of molybdenum, iron and vanadium doped titanium dioxide", Reaction Kinetics, Mechanisms and Catalysis, 2013

Publication

<1 %

33

Stephanie J. Jensen, Talgat M. Inerbaev, Dmitri S. Kilin. "Spin Unrestricted Excited State Relaxation Study of Vanadium(IV)-Doped Anatase", The Journal of Physical Chemistry C, 2016

Publication

<1 %

34

Jing Liqiang, Sun Xiaojun, Xin Baifu, Wang Baiqi, Cai Weimin, Fu Honggang. "The preparation and characterization of La doped TiO₂ nanoparticles and their photocatalytic activity", Journal of Solid State Chemistry, 2004

Publication

<1 %

35

Pourdayhimi, Parisa, Pei Wen Koh, Mohamed Mohd Salleh, Hadi Nur, and Siew Ling Lee. "Zinc Oxide Nanoparticles-Immobilized Mesoporous Hollow Silica Spheres for Photodegradation of Sodium Dodecylbenzenesulfonate", Australian Journal of Chemistry, 2016.

Publication

<1 %

36

www.preprints.org

Internet Source

<1 %

37

Chamnan Randorn, John T. S. Irvine, Peter Robertson. " Synthesis of Visible-Light-Activated Yellow Amorphous Photocatalyst ", International Journal of Photoenergy, 2008

Publication

<1 %

38

Nanostructure Science and Technology, 2010.

Publication

<1 %

39

Shuijin Lei, Xijie Gao, Di Cheng, Linfeng Fei, Wei Lu, Jianliang Zhou, Yanhe Xiao, Baochang Cheng, Yu Wang, Haitao Huang. " A Hierarchically Porous Hollow Structure of Layered Bi TiO F for Efficient Photocatalysis ", European Journal of Inorganic Chemistry, 2017

Publication

<1 %

40

bmcinfectdis.biomedcentral.com

Internet Source

<1 %

41

"Fundamentals of TiO₂ Photocatalysis. Consequences for Some Environmental Applications", Green Chemistry and Sustainable Technology, 2016.

Publication

<1 %

42

Jason L. Bronkema, Alexis T. Bell. "Mechanistic Studies of Methanol Oxidation to Formaldehyde on Isolated Vanadate Sites

<1 %

Supported on MCM-48", The Journal of
Physical Chemistry C, 2007

Publication

43

Nanostructure Science and Technology, 2016.

Publication

<1 %

44

Xi Liu, Jianjun Chen, Guochen Zhang, Yang Wu,
Puqing Shen, Lin Zhong, Yaoqiang Chen.

"Tuning the interactions among Ce, Pd and Rh
over Ce-modified Pd-Rh three-way catalyst for
exhaust treatment of natural gas vehicles",
Journal of Environmental Chemical
Engineering, 2021

Publication

<1 %

45

Xingtao Gao, Simon R. Bare, Bert M.
Weckhuysen, Israel E. Wachs. "In Situ
Spectroscopic Investigation of Molecular
Structures of Highly Dispersed Vanadium
Oxide on Silica under Various Conditions", The
Journal of Physical Chemistry B, 1998

Publication

<1 %

46

Yeh, C.. "Flame synthesis of titania particles
from titanium tetraisopropoxide in premixed
flames", Powder Technology, 20040716

Publication

<1 %

47

krclib.ncl.res.in

Internet Source

<1 %

48

lib.convdocs.org

Internet Source

<1 %

49

vdoc.pub

Internet Source

<1 %

50

www.scribd.com

Internet Source

<1 %

51

www.ung.si

Internet Source

<1 %

52

Halimaton Hamdan, Mohd Nazlan Mohd Muhid, Siew Ling Lee, Yin Yin Tan. "Visible Light Enabled V and Cr Doped Titania-Silica Aerogel Photocatalyst", International Journal of Chemical Reactor Engineering, 2009

Publication

<1 %

53

Jimmy C. Yu, Wingkei Ho, Jiaguo Yu, S. K. Hark, Kwansai Iu. " Effects of Trifluoroacetic Acid Modification on the Surface Microstructures and Photocatalytic Activity of Mesoporous TiO Thin Films ", Langmuir, 2003

Publication

<1 %

54

Nur Fatin Sulaiman, Siew Ling Lee, Susilawati Toemen, Wan Azelee Wan Abu Bakar. "Physicochemical characteristics of Cu/Zn/ γ -Al₂O₃ catalyst and its mechanistic study in transesterification for biodiesel production", Renewable Energy, 2020

Publication

<1 %

55

Ooi, Yee Khai, Leny Yuliati, Djoko Hartanto, Hadi Nur, and Siew Ling Lee. "Mesostructured TUD-C supported molybdena doped titania as high selective oxidative catalyst for olefins epoxidation at ambient condition", *Microporous and Mesoporous Materials*, 2016.

Publication

<1 %

56

P. C. Nagajyothi, S. V. Prabhakar Vattikuti, K. C. Devarayapalli, K. Yoo, Jaesool Shim, T. V. M. Sreekanth. "Green synthesis: Photocatalytic degradation of textile dyes using metal and metal oxide nanoparticles-latest trends and advancements", *Critical Reviews in Environmental Science and Technology*, 2019

Publication

<1 %

57

S. Chandra Shekar, Keshav Soni, Rajendra Bunkar, Manoj Sharma, Beer Singh, M.V.S. Suryanarayana, R. Vijayaraghavan. "Vapor phase catalytic degradation of bis(2-chloroethyl) ether on supported vanadia-titania catalyst", *Applied Catalysis B: Environmental*, 2011

Publication

<1 %

58

Wu, J.C.S.. "A visible-light response vanadium-doped titania nanocatalyst by sol-gel method", *Journal of Photochemistry & Photobiology, A: Chemistry*, 20040521

Publication

<1 %

59 Xiaobo Chen, Samuel S. Mao. "Titanium Dioxide Nanomaterials: Synthesis, Properties, Modifications, and Applications", Chemical Reviews, 2007

Publication

<1 %

60 Y. Berezniński, M. Jaroniec, M. Kruk, B. Buszewski. "Adsorption Characterization of Octyl Bonded Phases for High Performance Liquid Chromatography", Journal of Liquid Chromatography & Related Technologies, 2006

Publication

<1 %

61 docserv.uni-duesseldorf.de

Internet Source

<1 %

62 e-space.mmu.ac.uk

Internet Source

<1 %

63 escholarship.mcgill.ca

Internet Source

<1 %

64 etd.lib.metu.edu.tr

Internet Source

<1 %

65 jes.ecsdl.org

Internet Source

<1 %

66 scindeks-clanci.ceon.rs

Internet Source

<1 %

67 wrap.warwick.ac.uk

Internet Source

<1 %

68

www.carbon2013.org

Internet Source

<1 %

69

Jinwen Liu, Rong Han, Yan Zhao, Hongtao Wang, Wenjing Lu, Tongfeng Yu, Yaxin Zhang. "Enhanced Photoactivity of V-N Codoped TiO₂ Derived from a Two-Step Hydrothermal Procedure for the Degradation of PCP-Na under Visible Light Irradiation", *The Journal of Physical Chemistry C*, 2011

Publication

<1 %

70

Ting-Ke Tseng, Hsin Chu, Han-Hsuan Hsu. "The Catalytic Incineration of Trichloroethylene over γ -Alumina Supported Manganese Oxide Catalysts", *Journal of Environmental Science and Health, Part A*, 2003

Publication

<1 %

71

Tobaldi, D.M., R.C. Pullar, A.F. Gualtieri, M.P. Seabra, and J.A. Labrincha. "Sol-gel synthesis, characterisation and photocatalytic activity of pure, W-, Ag- and W/Ag co-doped TiO₂ nanopowders", *Chemical Engineering Journal*, 2013.

Publication

<1 %

72

"On Solar Hydrogen & Nanotechnology", Wiley, 2010

Publication

<1 %

73

Tianping Lv, Jianhong Zhao, Mingpeng Chen, Kaiyuan Shen, Dongming Zhang, Jin Zhang, Genlin Zhang, Qingju Liu. "Boosted Visible-Light Photodegradation of Methylene Blue by V and Co Co-Doped TiO₂", Materials, 2018

Publication

<1 %

Exclude quotes Off

Exclude matches Off

Exclude bibliography On

FINAL GRADE

GENERAL COMMENTS

/0

Instructor

PAGE 1

PAGE 2

PAGE 3

PAGE 4

PAGE 5

PAGE 6

PAGE 7

PAGE 8

PAGE 9

PAGE 10

PAGE 11

PAGE 12

PAGE 13

PAGE 14

PAGE 15

PAGE 16
