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Niobium Oxide Doped Titanium Dioxide Photocatalyst for Phenol Photodegradation

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Abstract

Phenolic compounds are highly toxic and contribute to water pollution, posing health risks with long-term exposure. To address this issue, heterogeneous photocatalysis, titanium dioxide (TiO_2) was chosen as a commonly used catalyst. However, TiO_2 is ineffective under visible light due to its wide band gap energy and thus leads to rapid recombination of electron-hole pairs. To enhance its performance, TiO_2 was doped with niobium oxide (Nb_2O_5), which had increased its photocatalytic activity under visible light. This study investigated the synthesis of Nb_2O_5-doped TiO_2 via sol-gel method. The X-ray diffractometry results revealed that all samples had crystallized in the anatase phase. DRUV-Vis spectroscopy confirmed the successful loading of Nb_2O_5 into TiO_2, resulting in a reduced band gap energy and enhanced photocatalytic performance. Amongst all the samples, 5wt% Nb_2O_5 doped TiO_2 recorded the highest phenol degradation activity (32%) under visible light irradiation.

Keywords Niobium oxide, TiO_2, photocatalyst, phenol photodegradation

1.0 INTRODUCTION

Phenolic compounds are a significant source of pollution in polluted water and can cause health issues with long-term exposure (Ge, Yoon, & Choi, 2018; Zhang, et al., 2023). Phenols are a type of organic pollutant that is either harmful to humans or resistant to certain microorganisms. As a result of its toxic nature and persistence in the environment, it can be considered as one of the most significant pollutants (Arfin, Sonawane, & Arshiya Tarannum, 2019; Ajmi, Bosu, & Rajamohan, 2024). When exposed to an excessive concentration of phenol, extensive damage can occur to organs such as the heart, kidneys, and liver (Anku, Mamo, & Govender, 2017). As a direct consequence of this, the process of removing phenolic compounds from both water resources and wastewater has received increased focus on a worldwide scale.

Heterogeneous photocatalysis is an advanced oxidation process (AOP) approach that has been discovered to successfully remove organic contaminants (Khaksar, Nazif, Taebi, & Shahghasemi, 2021). Furthermore, organic pollutants degrade in the absence of a broad band gap semiconductor that can boost reactions in the presence of UV radiation without being consumed in the whole reaction (Ling, et al., 2015). Due to remarkable crystalline and surface properties such as broad band gap, non-toxicity, and water stability, metal oxide-based semiconductors like TiO_2 have been developed and used as magnificent photocatalyst materials in AOP (Kumar, 2017).

TiO_2 appears to be a widely known photocatalyst in the AOPs, particularly for the mineralization of toxic and non-biodegradable organic pollutants in wastewater treatment. TiO_2 is a good heterogeneous photocatalyst due to its non-toxicity, good photochemical stability, good thermal stability, and relatively low material cost (Ling, Teng, Hatta, & Lee, 2021; Ooi, Yuliati, & Lee, 2016). TiO_2 is a semiconductor that has gap energies suitable for catalyzing a wide range of chemical processes (Ling, Yuliati, Lintang, & Lee, 2020). TiO_2 photocatalysts also have the potential to discolor and destroy organic colors in water and have been implemented in a variety of research to degrade gases that are hazardous to the environment (Bakbolat, et al., 2020). For instance, TiO_2 photocatalyst can be applied in the photodegradation of dyes such as Crystal Violet (Rabeie & Mahmoodi, 2023) as well as hazardous gases such as NO_x gases and formaldehyde (Park & Choi, 2022; Wang, et al., 2021). Regrettably, TiO_2 has a critical problem in that it is not a good effective photocatalyst under visible light radiation (Albertin, et al., 2023) because of its large band gap (3.2 eV), small surface area and limited photocatalytic activity of TiO_2 by fast electron-hole recombination (Ling, Teng, Hatta, & Lee, 2021; Chen, Koh, Ponnusamy, & Lee, 2022).

A few improvements, such as metal oxide doping, dye sensitization, and metal coupling, were performed in order to improve the photoactivity of TiO_2. Metal oxide doping (transition metal cations) was chosen as a more effective method of narrowing the band gap in TiO_2 (Lee, Khaw, & Ooi, 2016). According to the research, some of the strategies for modifying TiO_2 in order to achieve better activity include combining it with other semiconductor oxides or doping TiO_2 with a small amount of metals and non-metals (Ferrari-Lima, Marques, Gimenes, & Fernandes-Machado, 2015). The Nb_2O_5 nanoparticle has attracted a lot of attention because it has better adsorption and photocatalysis properties against emerging contaminants. Nb_2O_5 was chosen because it is a non-toxic and eco-friendly metal oxide that exhibits strong oxidation ability (Gomes, Olusegun, Gabriel, Costa, & Mohallem, 2023). Additionally, Nb_2O_5 was reported to decrease the band gap by modifying the structure of TiO_2 because transition metal ions are well known to be easily substituted into the lattice of TiO_2 (Ling, Teng, Hatta, & Lee, 2021). As documented, Nb_2O_5 could be a good catalyst due to its unique Lewis acid sites (LASs) as well as Bronsted-Lowry acid sites (BASs) (Su, Gao, Fornasiero, & Wang, 2021).

In this study, a series of Nb_2O_5 doped TiO_2 photocatalysts were synthesized. The physiochemical properties of the resulting photocatalysts were evaluated. The photocatalytic efficiency of the Nb_2O_5 photocatalysts towards the phenol degradation was investigated.

2.0 EXPERIMENTAL

2.1 Materials

Cetyltrimethylammonium bromide (CTAB), hydrochloric acid (HCl), niobium chloride ($NbCl_5$), tetrabutyl titanate (TBT) and titanium(IV) oxide were supplied from Sigma Aldrich, United States. Ethanol and phenol were purchased from Qrec, New Zealand and Scharlau, Spain. All the materials were used without any purification step in the research.

2.2 Preparation of materials

Niobium oxide doped TiO_2 was synthesized via the sol-gel method. 8 mL of ethanol was used to dissolve CTAB. TBT and HCl were added to the reaction mixture and further added with distilled water and ethanol. The reaction mixture was stirred for an hour at room temperature at 300 K and labeled as Solution A. Next, the niobium oxide (Solution B) was prepared by dissolving the niobium chloride with ethanol. After that, the niobium oxide solution was added dropwise into solution A. To ensure the homogeneity of the solution, the mixture of these two solutions was stirred for an hour at room temperature at 300 K. The solid gel was formed and then aged at room temperature at 300 K for 24 hours. The gel was then dried at 353 K for 8 hours and underwent a calcination process at 773 K for 3 hours. The samples were collected and labeled as $x$$Nb_2O_5$-$TiO_2$, where x refers to wt% of Nb_2O_5. For the comparison, the undoped TiO_2 was prepared with the same procedure but without the addition of Nb_2O_5 precursor. The sample was labelled as 100% TiO_2.

2.3 Characterization of materials

The characterizations of all synthesized samples were carried out by using several techniques. Fourier Transform Infrared (FTIR) (Thermo Scientific Nicolet iS10 Spectrometer) was used to determine the functional group of the samples with wavenumbers ranging from 450 to 4000 cm^{-1}. Diffuse Reflectance Ultraviolet-Visible (DRUV-Vis) analysis (Shimadzu UV-3600i Plus) was used for measuring and determining the band gap. $BaSO_4$ was used as reference substance for comparison with the synthesized photocatalyst. Lastly, for measuring the size and crystal structure of the synthesized Nb_2O_5–TiO_2, XRD (Bruker Advance D8) was used with the scans in the 2θ range of 10°– 80° with a step size of 0.02° and rate of 0.05°/sec. The diffraction patterns were compared with the standard ones simulated using VESTA software.

2.4 Photocatalytic degradation of phenol

The photocatalytic activity of the synthesized samples was tested by photodegradation of phenol under visible light irradiation. 0.1 g of sample was immersed and suspended in the 50 mL phenol solution with phenol concentration fixed at 50 ppm. The visible light source to irradiate the suspension was a halogen fiber optic light illuminator (BOTE, 150 W). The solution was stirred for 1 hour in dark conditions in order to establish adsorption equilibrium. The distance between the normal incidence of visible light and the solution was fixed at 25 cm. The solution was then irradiated under visible light for 5 hours and filtered using a membrane syringe filter. UV-Vis Spectrophotometer (Shimadzu UV-1800) was used to measure the concentration of filtrate. The experiment was carried out three times for every sample.

3.0 RESULTS AND DISCUSSION

Nb_2O_5-TiO_2 samples were synthesized via sol-gel techniques and calcined at 773 K for 3 hours, resulting in white pure TiO_2 powder and an increasingly pale-yellow color with higher Nb dopant concentrations as shown in Figure 1. This was due to the Ti-peroxo species as oxygen interstitials that introduced peroxo defect states above the TiO_2 valence band (Kong, Wang, Zheng, Zhang, & Liu, 2015).

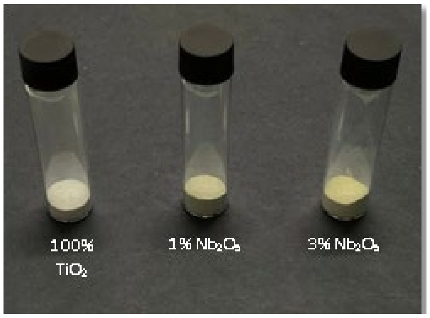

Figure 1 Photo showing white powder of 100% TiO_2 and pale yellow powder of 1 and 3 wt% of Nb_2O_5 doped TiO_2.

3.1 Characterization of TiO_2 and Nb_2O_5 doped TiO_2

3.1.1 Fourier Transform Infrared Spectroscopy

The FTIR spectra for three analyzed samples are shown in Figure 2. From the spectra, the broad stretching vibration mode of the hydroxyl group is observed in the range of 3410-3440 cm^{-1}, while the stretching vibrations of the O-H group are identified at 1628 cm^{-1}, indicating the presence of absorbed water in the calcined photocatalyst. The interaction of water with surface titanium atoms via hydrogen bonding explains these bands (Sacco, et al., 2020). For all the TiO_2-based samples, the broad peaks around 450 – 800 cm^{-1} correlated to the overlapping of the Ti-O-Ti peak Ti-O peak (Ling, Teng, Hatta, & Lee, 2021; Chelbi, et al., 2020). In the spectra of Nb_2O_5-based photocatalysts, there were no peaks discovered for Nb-O and Ti-Nb coordination bonds due to the insignificant loading amount of Nb_2O_5.

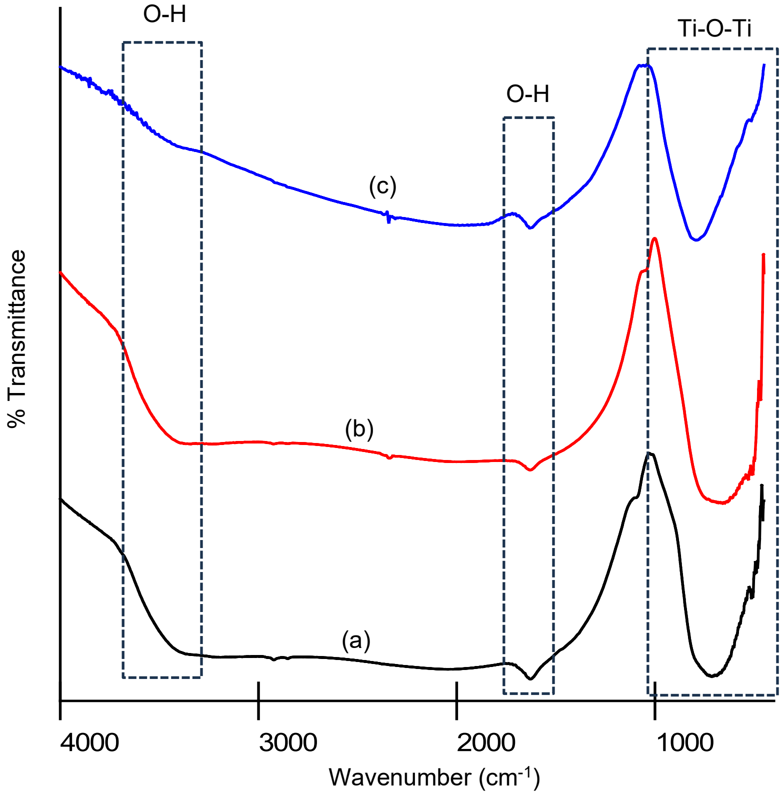

Figure 2 FTIR spectra of (a) TiO_2, (b) 1 wt% Nb_2O_5-TiO_2, and (c) 3 wt% Nb_2O_5-TiO_2

3.1.2 X-Ray Diffraction

Nb_2O_5-TiO_2 materials with different weight percentages of Nb_2O_5 (1% and 3%) were prepared and characterized, along with undoped TiO_2 for comparison. XRD analysis was conducted in the range of 20° to 80° with the peaks lying at $2\theta = 25.28°$ (101), $2\theta = 37.38°$ (004), $2\theta = 48.07°$ (200), $2\theta = 53.41°$ (105), and $2\theta = 55.09°$ (211). As illustrated in Figure 3, the XRD patterns showed peaks corresponding to the crystalline nature of the nanoparticles, with characteristic peaks indicating the anatase phase of TiO_2 (JCPDS 21-1272) (Lee, Khaw, & Ooi, 2016). The samples maintained their anatase phase even after calcination or doping with niobium oxides. No distinct peaks corresponding to niobium species were observed, possibly due to effective incorporation into the TiO_2 lattice, high dispersion, or the low concentration of niobium oxide present.

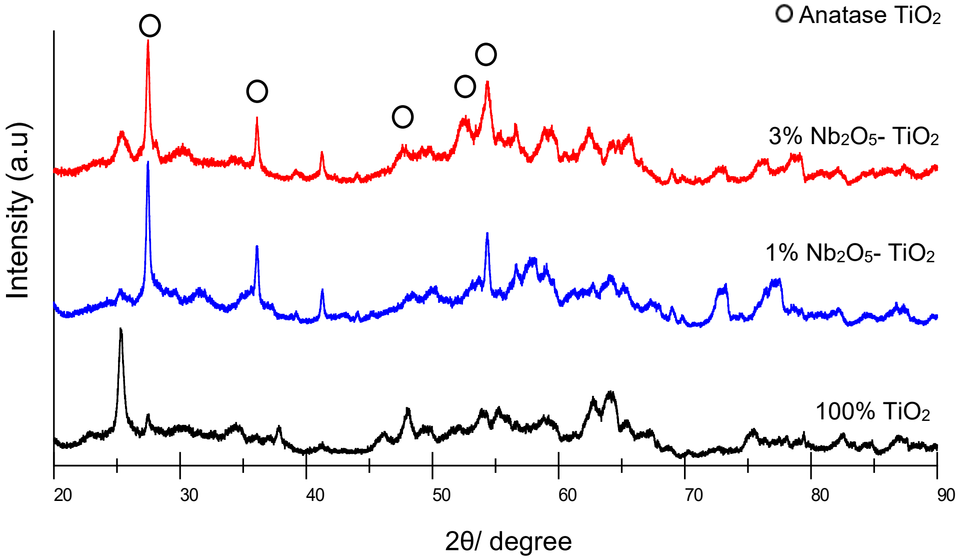

Figure 3 XRD diffractograms of TiO_2 and Nb_2O_5-TiO_2 samples

3.1.3 Diffuse reflectance ultraviolet-visible analysis

The DRUV-Vis spectroscopy was used to investigate the optical properties of the synthesized samples. For determining the optical band gap of the samples, the absorption spectra of DRUV-Vis were used by transforming them into Tauc plots. The UV-Vis spectrum of all the samples of TiO_2 and Nb_2O_5 doped TiO_2 are illustrated in Figure 4. As shown, pure TiO_2 exhibited a broad absorption band at around 320 – 400 nm. Besides, all the samples of Nb_2O_5 doped TiO_2 showed higher absorbance compared to pure TiO_2. It indicated that all the Nb_2O_5 doped TiO_2 samples were successfully synthesized (Choi, et al., 2022). The indirect band gap energy of the synthesized samples is shown in Figure 5. It shows that the band gap energy for pure TiO_2 was 3.10 eV. After the incorporation of Nb_2O_5 into TiO_2, the band gap energy of Nb_2O_5 doped TiO_2 is slightly reduced c.a. 3.00 eV. This could be due to the successful doping of Nb_2O_5 into TiO_2 as well as a narrow and significant band gap of Nb_2O_5 (Yan, Wu, Guan, & Li, 2014). The result found that doping TiO_2 with Nb_2O_5 alters its electronic structure, leading to a reduction in the band gap and increased absorption of visible light. The band gap energy represents the minimum energy required for electron transitions between the valence and conduction bands. With a lower band gap energy, TiO_2 can absorb lower-energy photons present in visible light. The smaller band gap observed in the 3% Nb_2O_5-TiO_2 sample suggests that Nb_2O_5 dopants modify the conduction band of TiO_2 by shifting it downward, possibly through the interaction between Nb and Ti states.

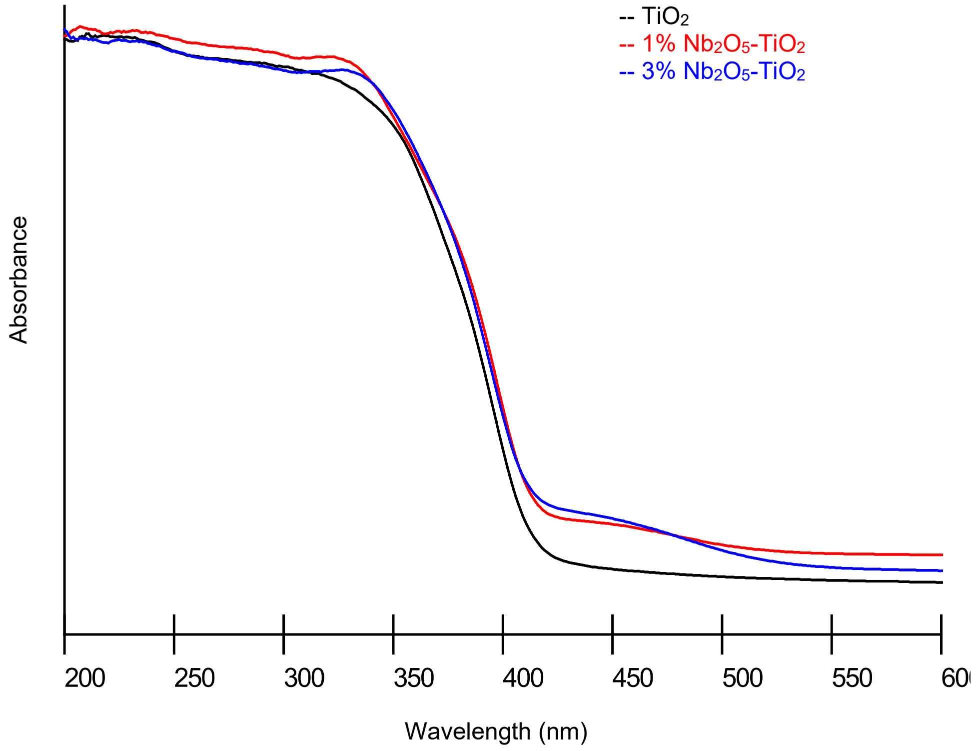

Figure 4 UV-Vis spectra of pure TiO_2 and Nb_2O_5-TiO_2 materials

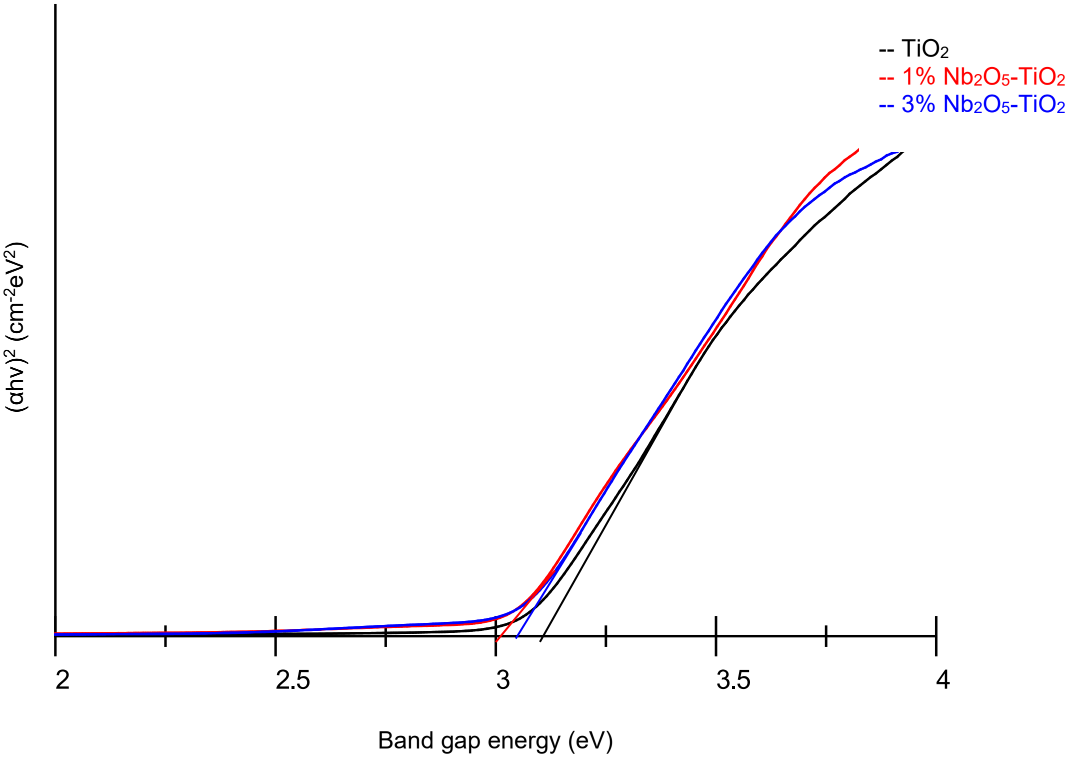

Figure 5 Tauc plots for band gap determination of pure TiO_2 and Nb_2O_5-TiO_2 materials

3.2 Photocatalytic degradation of phenol

The photocatalytic performance of commercial TiO_2, undoped TiO_2, and Nb_2O_5-TiO_2 samples (1 and 3 wt%) was evaluated by measuring the phenol photodegradation under visible light irradiation for 5 hours. The concentration of phenol before and after the reaction was determined using a calibration equation that was obtained which is $y = 0.0124x + 0.0218$ with $R^2 = 0.991$. The results, depicted in Figure 6, demonstrated that 100% TiO_2 exhibited the lowest photocatalytic activity, degrading only 15.2% of phenol. In contrast, the photocatalytic activity increased with higher niobium doping levels. Notably, the 3% Nb_2O_5-TiO_2 sample showed the highest degradation percentage, reaching 32.0%.

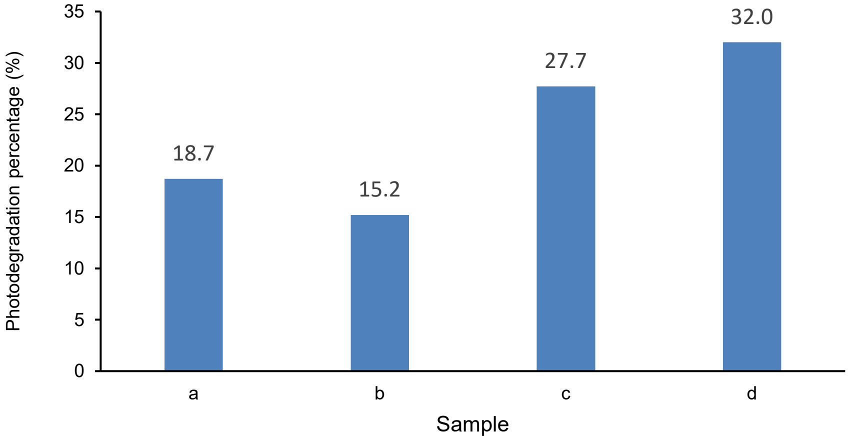

Figure 6 Photodegradation phenol over (a) commercial TiO_2, (b) 100% TiO_2, (c) 1% Nb_2O_5–TiO_2 and (d) 3% Nb_2O_5 – TiO_2.

Undoped TiO_2 demonstrated a phenol photodegradation of 15.2% after 5 hours of light irradiation, possibly due to photosensitization. Additionally, the bar chart indicated that commercial TiO_2 exhibited better photocatalytic activity (18.7%) compared to 100% TiO_2 (15.2%). This difference was attributed to the well-controlled particle size and morphology of commercial TiO_2, which leads to nanoparticles with a narrow size distribution, specific shapes, high surface area, and porosity. These characteristics provide more active sites for reactant adsorption and enhance reactant and product diffusion, resulting in improved photocatalytic activity.

The current results showed that the introduction of Nb_2O_5 to TiO_2 resulted in enhanced photocatalytic activity compared to undoped TiO_2. It was believed that the Nb_2O_5 doping on TiO_2 could enhance the electron-hole separation process since addition of Nb_2O_5 dopant might have favored the migration process of photogenerated electrons to niobium (Lee, Khaw, & Ooi, 2016).

4.0 CONCLUSION

A series of Nb_2O_5 doped TiO_2 was successfully prepared using a sol-gel technique at room temperature with different weight percentage of Nb_2O_5 (1 and 3 wt%). The presence of Nb_2O_5 doped TiO_2 was evidenced by the DRUV-Vis, FTIR and XRD analyses with the TiO_2 and Nb_2O_5 functional groups existed as well as the reduced band gap of the resulting materials. The photocatalytic performance of Nb_2O_5 doped TiO_2 was significantly improved compared to the undoped TiO_2, suggesting that the Nb_2O_5 is a promising dopant for TiO_2. The highest photocatalytic activity was achieved on sample 3 wt% Nb_2O_5 doped TiO_2 under visible light irradiation in 5 h. It was concluded that Nb_2O_5 is an effective dopant for TiO_2 in the photodegradation of phenol, suggesting potential of Nb_2O_5 doped TiO_2 as an efficient photocatalyst.

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