Effect of iron loading onto mesoporous titania nanoparticles and its photoactivity

N A Marfur, N F Jaafar* and N H H M Habibullah

School of Chemical Sciences, Universiti Sains Malaysia, 11800 USM Penang, Malaysia

*nurfarhana@usm.my

Abstract. Titania is proven to be one of the best catalysts for various pollutant degradations. However, it can only be activated under UV light. This research was conducted to further enhance the photoactivity of titania under visible light irradiation by doping with iron metal. Different weight loadings of Fe (3, 5, 7 and 10 wt.%) supported on mesoporous titania nanoparticles (MT) were synthesised via a facile in-situ electrochemical method and denoted as 3FMT, 5FMT, 7FMT and 10FMT to degrade 2-chlorophenol (2-CP). These catalysts were characterised by XRD, FTIR and UV-Vis DRS. The photocatalytic activity of 3FMT was the most effective with 98% degradation probably due to its lowest band gap energy. Therefore, this study showed great enhancement in the photoactivity of the catalysts especially under visible light irradiation by lowering their band gaps.

1. Introduction

In the past decades, rapid development in industries has resulted in numerous issues regarding environmental pollution [1]. Through heavy industrialisation, numerous amounts of toxic and carcinogenic pollutants pose a great threat to human and aquatic life [2]. According to Olaniran et al., a major group of wastewater pollutants known as chlorinated phenols are heavily used in various industrial processes such as pesticides, herbicides, fungicides, disinfectants, antiseptics, wood and glue preservatives, paints, solvents and dye intermediates in the textile industries. Among the family of chlorinated phenols, 2-chlorophenol (2-CP) is the most volatile derivative [3-4].

Advanced Oxidation Process (AOP) utilises heterogeneous photocatalytic inorganic semiconductors to remove hazardous pollutants and chemical contaminants [5]. Among numerous semiconductors that have been synthesised and studied as photocatalysts, TiO$_2$ is rising in popularity among researchers due to some interesting aspects such as chemical inertness, high stability, non-toxicity and low cost [6]. However, Chong et al., have reported that large band gap in the anatase crystalline phase, low surface area and high photogenerated electron-hole recombination rate have limited the photocatalytic performance of TiO$_2$ [7].

Incorporating transition elements as dopant in the mesoporous titania nanoparticles (MT) structure was found to be a fascinating approach and iron (Fe) is a promising candidate due to its half-filled electron configuration which can potentially prevent fast electron hole recombination rate [8]. However, it was reported that excessive metal loading could promote recombination which furthermore might agglomerate and block the pores resulting in the reduction of light penetration and its photoactivity [9]. Therefore, attempts were made to modify MT by introducing various weight
loadings of Fe (3-10wt.%) as dopants onto MT structures via a facile in-situ electrochemical method and the optimum amount of Fe was determined. In this study, the band gaps which give major contribution to the photoactivity were expected to be greatly lowered and made suitable to perform under visible light irradiation.

2. Experimental

2.1. Materials and apparatus
Fe and Pt plates with 99 % purity acted as electrodes using the facile electrochemical method and were attained from Nilaco, Japan. N,N-Dimethylformamide (DMF), propanol, and hydrochloric acid were obtained from MERCK, Malaysia. Sodium dodecyl sulphate (SDS) was obtained from SYSTERM. Acetone was attained from HmbG Chemical whereas titanium isopropoxide (TTIP) was purchased from Sigma Aldrich. Naphthalene was obtained from Fluka Chemical. Sodium hydroxide and 28 % ammonium solution were purchased from QRECTM whereas 2-CP was bought from Alfa Aesar, Germany with 99 % purity. Tetraethylammonium perchlorate (TEAP), which acted as a supporting electrolyte was synthesised based on the method reported by Jalil et al. [10]. All the chemicals were of analytical grade and were used without any further purification.

2.2. Catalysts preparation
MT was prepared using the microwave approach. 4.68 g of SDS surfactant was added into 720 mL of distilled water, 120 mL of propanol and 29 mL of 28 % ammonia solution. The mixture was stirred at 323 K in a water bath. After half an hour, 5.7 mL of TTIP precursor was added and stirred for 2 h at 353 K. Then, the solution was transferred into a beaker and heated using a microwave with a power of 450 W. Intermittent heating was continued until MT sol-gel was obtained and dried overnight in an oven followed by calcination at 873 K for 3 h.

After that, Fe was loaded onto MT via electrochemical means. 20 mL of DMF solution was added into a one-compartment cell equipped with a Pt plate and Fe plate. 1.5 g of MT, 0.46 g of 0.1 M TEAP and calculated mass of naphthalene were also added into the cell. Electrolysis was performed under constant current of 24 mA/cm² at 303 K and continuously stirred. 3, 5, 7 and 10 wt % Fe loaded onto MT (FMT) were prepared by adjusting the electrolysis time according to the Faraday’s law of electrolysis. The mixture was then dried using an oil bath until the powder formed before being kept in the oven overnight followed by calcination at 873 K for 3 h.

2.3. Catalysts characterization
The crystalline structures of the catalysts were identified using a Bruker Advance D8 X-ray powder diffractometer (XRD). The phases were determined with the help of the Joint Committee on Power Diffraction Standard (JCPDS) files. UV-Vis DRS (Perkin Elmer Lambda 900) spectrophotometer was used to measure the diffuse reflectance of the catalyst in air at room temperature. The chemical functional groups present in the catalysts were identified by FTIR spectroscopy (Perkin Elmer Spectrum 2000 FT-IR). IR absorbance data were obtained over a range of wavenumbers from 500 to 4000 cm⁻¹.

2.4. Catalysts photoactivity
The photoactivity of the catalyst was tested through the degradation of 2-CP. Reactions were performed in a reactor using a fluorescence lamp as the light source. About 0.0750 g of the catalyst was put into 200 mL of 10 ppm 2-CP solution with initial pH 5. The blank solution was taken out before adding the photocatalyst. The solution was also stirred continuously at room temperature and left under dark conditions for 2 h before being exposed to light for 6 h. The solution was then taken out and checked every half an hour before being analysed using UV-Vis spectrophotometer at a wavelength of 274.5 nm. Concentration of the solution right before being exposed to light was used as the initial concentration to calculate percentage degradation using this equation:
where \( C_0 \) and \( C_t \) are the initial concentration and the concentration at time of solution, correspondingly.

3. Results and discussion

3.1. Catalysts characterization

Figure 1 shows XRD patterns of each catalyst. Distinctive peaks were noticed at 25.3° (101), 36.9° (103), 37.9° (004), 38.7° (112), 48.1° (200), 53.9° (105), 55.1° (211) and 62.8° (204) which correspond to anatase TiO\(_2\) (JCPDS file no. 01-086-1157). From the result, it can be deduced that peak intensity of TiO\(_2\) decreased as weight loadings of Fe onto MT increased. According to Karim et al., the degree of orderliness and mesopore uniformity of MT had moderately reduced after Fe loaded onto MT. However, the catalyst structure was not really affected by this modification. Diffraction peak at 35.2° was detected which indicated the presence of Fe in the MT lattice [11]. The new peak increased in intensity as Fe loading increased. The particle size of materials determined using Debye-Scherrer equation:

\[
D = \frac{k\lambda}{\beta \cos \theta}
\]

where \( D \) is the particle size, \( \lambda \) is the wavelength of the X-ray radiation (Cu K\(_\alpha\) = 0.1542 nm), \( k \) is the shape factor \((k=0.94)\), \( \beta \) is the line width at half-maximum height, and \( \theta \) is the angular position of the maximum peak, \( 2\theta = 25° \). The sizes of particle for MT, 3FMT, 5FMT, 7FMT and 10FMT were 4.4 nm, 4.7 nm, 3.5 nm, 4.1 nm and 4.6 nm correspondingly which proved that these photocatalysts were reduced in size as Fe weight loading escalated.

Figure 2 shows band gap energy of each material. According to Ozer et al., high recombination rate of electron-hole resulted from wide band gap in MT which affected the stabilisation of the
photocarrier charge in the large catalyst and limited the photoactivity [12]. The band gap energies were determined using this equation:

\[ eV = \frac{hc}{\lambda} \]

where \( h \) is Planck's constant \((6.63 \times 10^{-3} \text{ m}^2 \text{ kg/s})\), \( c \) is speed of light \((3 \times 10^8 \text{ m/s})\) and \( \lambda \) is the wavelength value proportional to the intersection point of the vertical and horizontal part of the spectra. Based on the result, it can be concluded that MT (3.2 eV) band gap was greatly reduced after Fe was added into the MT framework. According to Li et al., they proposed that with the addition of transition metals cation like Fe as a dopant into the TiO\(_2\) framework, electron-hole recombination rate could be reduced and its photoactivity would show great improvement [13].

The functional groups of these catalysts were supported by FTIR. From the FTIR spectra in figure 3B, these materials show a wide absorption band around 3200 to 3900 cm\(^{-1}\). This band indicated the hydroxyl (OH) group that was chemisorbed onto the surface of the titania structure [14]. The hydroxyl band had also reduced as Fe weight loading increased. According to Hadjiivanov et al., the loaded Fe atoms might change the initial titania structure through perturbation [15]. As shown in figure 3A, the absorption band at 1300 cm\(^{-1}\) showed by these materials corresponded with Ti-O-Ti asymmetric stretching as well as bending vibrations while the band at 650 cm\(^{-1}\) revealed itself as one of the identities for the titanium tetrahedral structure [16]. Besides, both absorption bands intensity at 1300 and 650 cm\(^{-1}\) were reduced when weight loadings of Fe onto MT increased.

3.2. Catalysts photoactivity

Photoactivities of these materials upon degradation of 2-CP under visible light irradiation is as shown in figure 4. 3FMT have exhibited the highest degradation (98 %) followed by MT (80 %), 10FMT (73 %), P25 (60 %), 7FMT (57 %) and 5FMT (52 %). This is in agreement with the characterisation results. The intensity or trend from XRD and FTIR results only showed slight differences between the catalysts. However, their band gap exhibited significant difference for the catalysts. Therefore, it can be concluded that band gap was the major factor in this study which improved the photocatalytic degradation of 2-chlorophenols. This also can be seen where 3FMT with the lowest band gap demonstrated the highest degradation. On the other hand, as the percentage iron loading increased, the band gap became higher so the percentage degradation was reduced. Great efficiency exhibited by 3FMT was due to the synergistic effect among Fe and MT [1]. As published by Hoffman et al. and Piera et al., iron (III) ions have the potential to serve as shallow traps in a titania lattice framework besides being lifted the MT electron-hole also possesses recombination properties that reduces the band gap energy. The best photocatalytic properties could be attained by adding dopant at an adequately low amount for example 3 % of iron metal [17-19].

Photocatalytic performance of this material is mainly governed by the pH solution. In order to obtain the best pH for the photocatalyst environment, photocatalytic degradation with different pH ranging from 3 to 11 was carried out. Based on figure 5, photoactivity of 3FMT shows the highest degradation (98 %) in a pH 5 solution followed by pH 3, 7, 9 and 11 with a percentage degradation of 65 %, 25 %, 10 % and 5 %, correspondingly. Therefore, it can be deduced that 3FMT showed the best photocatalytic performance in an acidic environment. Generally, points zero charge (pHzpc) of the catalyst will determine the optimum pH for the reaction. The suitable pH reaction related to amphoteric performance of the catalyst depends on pHzpc for the best catalyst (3FMT) which was found to be at pH 6.2 (figure not shown) as well as organic pollutants charge. Therefore, strong electrostatic force between the positively charged catalysts surface and negatively charged 2-CP contribute to high photoactivity [11].
Figure 2: UV-vis spectra of (A) 3FMT, (B) 5FMT, (C) 7FMT and (D) 10FMT

Figure 6 shows photoactivity of 3FMT with different initial concentration of 2-CP from 10 to 100 mg L\(^{-1}\). 10 mg L\(^{-1}\) showed the best photoactivity (98 %) upon 2-CP. This resulted from 10 mg L\(^{-1}\) concentration which is expected to have fewer molecules so more light could penetrate the photocatalyst surface thus enhancing the photocatalytic performance. Nevertheless, as the initial concentration of 2-CP escalated, the photoactivity declined. It could be concluded that the raised amount of pollutant molecules has inhibited the light penetration towards materials resulting in remarkable depletion of hydroxyl ions and photoactivity [20-21].
Figure 3: (A) FTIR spectra in region 1300-500 cm\(^{-1}\); and (B) FTIR spectra in region 4000-2500 cm\(^{-1}\) of (a) MT, (b) 3FMT, (c) 5FMT, (d) 7FMT and (e) 10FMT.

Figure 4: Photocatalytic degradation of (a) P25, (b) MT, (c) 3FMT, (d) 5FMT, (e) 7FMT and (f) 10FMT. (\(C_{2,CP} = 10 \text{ mg L}^{-1}\), pH=5, W=0.375 g L\(^{-1}\), t = 8 h, T=303 K).
Fig. 5. Percentage degradation of 2-CP using 3FMT under different pH (C_{2,CP} = 10 \text{ mg L}^{-1}, W=0.375 \text{ g L}^{-1}, t=8 \text{ h}, T=303 \text{ K}).

Figure 6: Percentage degradation of 2-CP using 3FMT at different initial concentration (pH=5, W=0.375 \text{ g L}^{-1}, t=8 \text{ h}, T=303 \text{ K}).

Figure 7 shows the percentage degradation using varied dosage of 3FMT which were 0.100, 0.260, 0.375, 0.490 and 0.600 \text{ g L}^{-1}. This parameter was intensely investigated to optimise the catalyst reaction. From this study, it has been confirmed that 3FMT performed the best using amount of 0.375 \text{ g L}^{-1} (98 \%) followed by 0.490 \text{ g L}^{-1} (80 \%), 0.260 \text{ g L}^{-1} (65 \%), 0.600 \text{ g L}^{-1} (70 \%) and lastly
0.100 g L\(^{-1}\) (42 %). According to Zhou et al., low amounts of surface active sites on the photocatalyst might have resulted from the accumulation of materials which could reduce photocatalytic performance [22]. In addition, increasing the dosage to more than 0.375 g L\(^{-1}\) could give negative impact towards the suspension in the pollutant in terms of its turbidity which limits the light exposure on the material surface.

![Percentage degradation of 2-CP using different 3FMT dosages](image)

Figure 7: Percentage degradation of 2-CP using different 3FMT dosages (C\(_{2-CP}\) = 10 mg L\(^{-1}\), pH=5, \(t = 8\) h, T=303 K).

4. **Conclusion**

In this study, various loadings of Fe (3,5,7 and 10 wt.%) were successfully introduced into mesoporous titania nanoparticles (MT) via a facile in-situ electrochemical method. The FMT catalysts were characterised using XRD, FTIR and UV-Vis DRS. The XRD results showed that the TiO\(_2\) peak decreased in intensity as the weight loadings of Fe onto MT increased. There was also a new peak formed which increased in intensity with the increasing weight loadings of Fe. Several parameters were chosen and studied using FMT catalysts for the photocatalytic degradation of 2-CP which included pH of the pollutant, concentration of the pollutant and dosage of the catalyst. Based on the results, it was found that 3FMT was the best as it yielded the highest degradation of 2-CP among other catalysts. From this study, the band gaps which give major effect to photoactivity were greatly lowered and made highly suitable to perform under visible light irradiation. This is consistent with the lowest band gap energy data that was obtained for the 3FMT.

5. **Acknowledgement**

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