Photodegradation of phenol by N-Doped TiO₂ anatase/rutile nanorods assembled microsphere under UV and visible light irradiation

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HIGHLIGHTS
• Synthesis of N-Doped TiO₂ Anatase/Rutile Nanorods via simple preparation method.
• Direct incorporation of HNO₃ as the nitrogen dopant source.
• The photocatalytic properties were studied upon UV and visible light irradiation.
• The optimum calcination temperature is 400 °C for high photocatalytic activity.

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ABSTRACT
N-doped TiO₂ anatase/rutile nanorods assembled microspheres were successfully synthesized via a simple and direct sol–gel method containing titanium-n-butoxide Ti(OBu)₄ as a precursor material, nitric acid as a catalyst, and isopropanol as a solvent. By manipulating calcination temperature, the photocatalyst consisting of different phase compositions of anatase and rutile was obtained. The prepared TiO₂ nanoparticles were characterized by means of x-ray diffraction (XRD), field emission scanning microscope (FESEM), atomic force microscopy (AFM), Brunauer–Emmett–Teller (BET) analysis, UV–Vis–NIR spectroscopy, and fourier transform infrared (FTIR). The results from UV–Vis–NIR spectroscopy and FTIR revealed the direct incorporation of nitrogen in TiO₂ lattice since visible absorption capability was observed at 400–600 nm. XPS study indicated the incorporation of nitrogen as dopant in TiO₂ at binding energies of 396.8, 397.5, 398.7, 399.8, and 401 eV. Calcination temperature was observed to have a great influence on the photocatalytic activity of the TiO₂ nanorods. The photocatalytic activity of the prepared mixed phase of anatase/rutile TiO₂ nanoparticles was measured by photodegradation phenol in an aqueous solution under UV and visible irradiations. N-doped TiO₂ anatase/rutile nanorods assembled microsphere (consists of 38.3% anatase and 61.7% rutile) that was prepared at 400 °C exhibited the highest photocatalytic activity after irradiated under visible and UV light for 540 min. The high performance of photocatalyst materials could be obtained by adopting a judicious combination of anatase/rutile prepared at optimum calcination conditions.

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1. Introduction
The ability of TiO₂ semiconductor to degrade organic and inorganic pollutants comes from redox environment that is generated from photoactivation; and this makes it intensively utilized as a photocatalyst in wastewater treatment [1–3]. The photoactivation of TiO₂ photocatalyst occurs when the absorption of UV irradiation onto TiO₂ particles surface takes place. The UV irradiation absorption can be equal or higher than the band gap value of 3.2 eV for anatase or 3.0 eV for rutile [4,5]. TiO₂ exists in three distinct poly-morphs, which are anatase, rutile (both tetragonal crystal systems), and brookite (orthorhombic crystal system) [6,7]. A previous study on the band gap alignment of rutile and anatase TiO₂ has proven that the mixed phase of anatase/rutile TiO₂ has synergistic effects and higher photocatalytic activity as compared to pure phase of either in anatase or rutile [4]. Degussa P25 and Aeroxide TiO₂ P25

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are the common commercial mixed phases of anatase/rutile TiO₂, containing about 80% anatase and 20% rutile. The reason for the synergistic effects of the mixed phase of anatase/rutile TiO₂ nanoparticles in photocatalytic properties, however, still remains elusive. It is believed that the mixed phase of anatase/rutile TiO₂ can improve the charge carrier separation through electron trapping in rutile and consequently reduce the electron recombination. As a result, the formation of radical species for oxidation of substrate molecules can be maintained [8].

A major drawback of TiO₂ pure is its large band gap, which means it can only be activated under UV region (λ ≤ 387 nm), thus limiting the practical efficiency for solar applications [9]. Therefore, it is important to develop photocatalyst that can be utilized under visible light. Currently, increasing attention has been paid to the doping of TiO₂ with non-metal atoms since it provide a promising way to avoid deteriorating thermal stability of the TiO₂ lattice structure [10]. An effective way to narrow the band gap is to dope TiO₂ with non-metal elements such as B, S, C, F, N, F, Cl, Br and I [11,12]. However, nitrogen has been found to be one of the promising non-metal dopant materials for TiO₂ lattice to induce visible absorption [13–15]. The main reasons of utilizing nitrogen as the dopant material are due to its comparable atomic size with oxygen, small ionization energy, eco-friendly, higher stability and simple synthesis methods [14,16,17]. In a present study conducted by Hu and co-worker (2014), N-doped anatase/rutile TiO₂ hybrid material was synthesized in low-temperature by direct nitridization in order to enhance photocactivity under UV and visible light irradiations [11]. The substitution of lattice oxygen via nitrogen doping in TiO₂ lattice crystals leads to narrowed band gap and facilitated visible light absorption capability [14]. On top of that, nitrogen doping also inhibited the recombination of the photoinduced carriers and therefore increased the quantum efficiency of TiO₂ photocatalyst [11,14,18]. Basically, this approach has expanded the versatility of TiO₂ photocatalyst in a broader range of UV and visible regions. The combined effects of N-doping and synergistic effects have improved the photocatalytic activity of TiO₂ in the mineralization of hazardous pollutants.

Recently, there are several advanced synthesis method have been applied to prepared visible light active TiO₂ included Flame Spray Pyrolysis (FSP), sputtering technique, Angle Deposition (AOD) technique, Successive Ion Layer Adsorption and Reaction (SILAR), and Flame Spray Pyrolysis (FSP) [19–22]. The common defect of these techniques is the requirement of complicated and relatively expensive equipment. The development of novel TiO₂ photocatalyst with enhanced UV and visible light activity via economic, simple and direct synthetic method has become necessitous. Sol–gel method is one of the most prominent methods used to prepare mixed phase of anatase/rutile TiO₂ nanoparticles due to its simplicity and low equipment requirements. The preparation of TiO₂ from sol–gel had some advantages, such as the production of high purity nanocrystalline through precipitation and the flexibility to control the synthesis process [23]. There are three main chemical reagents required in the preparation of TiO₂ via sol–gel method, which are a precursor or the starting material for Ti source, an acid catalyst, and a solvent as dispersing media. The common precursors used for the preparation of anatase nanocrystalline are titanium–n-butoxide [23–25], titanium (IV) isopropoxide [26,27], and tetrabutyl ortho-titanate [28]. The highly crystalline TiO₂ nanoparticles can be prepared via sol–gel method, and followed by heat treatment that ranges from 0 to 600 °C [25,29]. It has been reported that the high quality of mixed phase of anatase/rutile TiO₂ nanoparticles, which contributes to high photocatalytic activity, can also be obtained by manipulating the types of reagents and heat treatment conditions [7,30,31]. However, to the best of our knowledge, there is hardly a report on the simple and direct preparation of nitrogen doped anatase–rutile mixed phase TiO₂ nanostructures [32,33].

Therefore, the aim of this research was to prepare N-Doped TiO₂ anatase/rutile nanorods assembled microspheres with high photocatalytic properties in UV and visible regions via simple and direct sol–gel method by manipulation of calcination temperature. In this study, titanium-n-butoxide, Ti(ÖBu)₄ was used as the Ti precursor, nitric acid as the catalyst, and isopropanol as the dispersing media. The introduction of nitrogen in TiO₂ lattice crystal was directly doped during the sol–gel preparation at low temperature. The photocatalytic activity of the prepared TiO₂ nanoparticles was evaluated by using the photodegradation of phenol in aqueous solution under UV and visible light irradiations.

2. Experimental

2.1. Materials

Titanium-n-butoxide Ti(ÖBu)₄ from Sigma–Aldrich was used as the titanium precursor. Nitric acid (HNO₃ 65%) and isopropanol (C₃H₇OH) were purchased from QReC Chemicals. In this study, HNO₃ was used as the catalyst and also as the nitrogen source. Isopropanol and distilled water were used as the dispersing media. Commercial TiO₂ consisting of Degussa P25 (TF25) and pure anatase purchased from Sigma–Aldrich (TAA) were used in the control experiment. All the chemicals used were of analytical reagent grade and used as received.

2.2. Photocatalyst preparation

A sol–gel method was applied to synthesize N-doped TiO₂ anatase/rutile nanorods assembled microsphere. Titanium precursor (Ti(ÖBu)₄) was added dropwise into the isopropanol solution under magnetic stirring until a homogeneous mixture was obtained. The mixture was then added dropwise into distilled water to promote hydrolysis of titanium precursor. The time for hydrolysis-polymerization process to occur was fixed for 30 min under vigorous magnetic stirring. Then, HNO₃ was added dropwise into the mixture and vigorously stirred for approximately 30 min. The resultant mixture followed a volume ratio of 25:8:200:3 for Ti(ÖBu)₄: C₃H₇OH:H₂O:HNO₃. The prepared mixture was then aged in tight air for several days until the formation of yellowish sol–gel was observed. The yellowish sol–gel was then dried at 75 °C for 74 h in a vacuum oven until yellowish powder was obtained and it was denoted as T75. The dried sample was subjected to calcination treatment at 200, 400, 600, 800 °C and denoted as T200, T400, T600, and T800, respectively. Calcination treatment was carried out in the furnace at 5 °C min⁻¹ of heating rate for 2 h.

2.3. Characterization

X-ray diffraction (XRD) was used to analyse the crystallinity of the TiO₂ samples. Measurements were carried out at 40 kV and 40 mA, employing a CuKα radiation at a wavelength of 0.15418 nm. The diffracted intensity was measured at the scan range of 2θ = 20–80° with a scan step speed of 1°/min. The average sizes of the crystallites of two main TiO₂ crystalline phases at crystal plane (101) anatase and (110) rutile were estimated using Scherrer equation [30].

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

(1)

where K is the Scherrer constant (usually 0.89), β, λ and θ are the full-width-at-half-maximum (FWHM) in radian [34], the radiation wavelength, and the incident angle of the X-rays, respectively.
The analysis of Fourier transform infrared (FTIR) spectroscopy was performed using Perkin Elmer FT-IR ATR spectrophotometer with diamond ATR sampling accessory. The spectrum of each sample was scanned with the wavenumber ranging from 4000 to 650 cm⁻¹. The surface morphologies of the catalyst samples were characterized using field emission electron scanning microscopy (FESEM) and atomic force microscopy (AFM). The surface areas were calculated by using the BET single point method. The UV–Vis spectra were used to indicate the optical responses of the prepared TiO₂ nanoparticles at different calcination temperatures. All the optical absorption spectra of the samples were recorded in a wavelength ranging between 200 and 600 nm, using a UV–Vis–NIR spectrophotometer Model UV-3101PC Shimadzu.

2.4. Photocatalytic activity measurement

The photocatalytic activity of the prepared N-doped TiO₂ nanoparticles was evaluated via degradation of phenol in aqueous solution under both UV and visible irradiations. The photocatalyst (0.3 g) was added into 400 ml of 50 ppm phenol solution and sonicated for 15 min. The mixture was stirred continuously with a magnetic stirrer in the dark for 1 h to achieve adsorption/desorption equilibrium. After that, 3 ml of the mixture was taken as a blank sample prior to irradiation and was treated as the initial concentration of phenol (C₀). Then, the mixture was irradiated using ultraviolet (UV) lamp (Vilber Laurmat, λ = 312 nm, 30 W) and visible lamp (light-emitting diode (LED) lamp, λ > 420 nm, 30 W). An air diffuser was used to provide sufficient O₂ for the reaction. The suspensions (3 ml) were then collected at 30 min interval using ultrathin polyamide syringe filter to eliminate excess catalysts prior to analysis. The clear liquid from each suspension was subjected to UV–Vis spectroscopy to measure the concentration change of phenol throughout the experiment at 296.35 nm. The photocatalytic activity was expressed in the percentages of phenol degradation according to the following equation:

\[
\text{Degradation of phenol} = \frac{C_0 - C_t}{C_t} \times 100\% \quad (2)
\]

where \( C_0 \) is the initial concentration at time \( t = 0 \), and \( C_t \) is the concentration at time \( t \) (30, 60, 90, 120, 150, 180, 210, 240, 270, and 300 min).

A similar experiment was carried out for the commercial anatase TiO₂ from Sigma–Aldrich (TAA) and Degussa P25 (TP25) under UV and visible irradiations. A blank experiment was also carried out using direct photolysis of phenol, irradiated under UV and visible light and without the presence of photocatalyst.

3. Results and discussion

3.1. X-ray diffraction

XRD technique is often used to identify the existence of crystalline phase in TiO₂ nanoparticles. Fig. 1 shows the XRD pattern of the TiO₂ prepared at different calcination temperatures. As presented in Fig. 1, the intensity of XRD pattern of T75 increased with the increase of calcination temperature from 200 to 800 °C. Generally, high intensity of the XRD pattern exhibits high crystallinity. By increasing the calcination temperature up to 800 °C, pure phase of rutile TiO₂ with high crystallinity was formed completely as the disappearance of (101) diffraction peak was observed. Hence, it can be concluded that the phase of transition of TiO₂ nanoparticles depends on the calcination temperature. This phase transition was irreversible; in other words, rutile was prohibited to transform back into the anatase phase although the rutile was recalcined at a lower temperature [30,35]. In the present work, pure and highly crystalline rutile TiO₂ nanoparticles were obtained at a calcination temperature of 800 °C. Small traces of diffraction peak signals of the brookite phase were observed in T75, T200, and T400 samples at 2θ of 30.77°, 30.82°, and 30.85°, respectively. It was demonstrated that the crystallinity of the mixed phase of anatase/rutile TiO₂ was enhanced gradually as a function of calcination temperature. It was clearly shown by the intensity of the diffraction peak, which became higher and sharper. The intensity of the diffraction peak of anatase plane at (101) decreased significantly, while the diffraction peak of rutile crystal plane at (110) increased for increasing calcination temperature.

Table 1 presents a summary on crystalline properties of the TiO₂ nanoparticles prepared at different calcination temperatures based on the XRD pattern. The weight fraction (WR) between anatase and rutile was calculated by using the following equation:

\[
WR = \frac{Ar}{0.884Aa + Ar} \quad (3)
\]
where $A_r$ is the integrated intensity of the rutile (110) peak and $A_a$ is the integrated intensity of the anatase (101) peak [36]. It can be seen that T75 exhibited a mixed phase of anatase/rutile TiO$_2$ at the drying stage as low as 75 °C, with the percentages of anatase and rutile were 95% and 5%, respectively. Although the mixed phase of anatase/rutile TiO$_2$ can be formed at 75 °C, the crystallinity was low.

The average crystallite sizes of the anatase and rutile in each sample were estimated using the Scherrer equation. According to Table 1, the average crystallite sizes of anatase and rutile increased as the calcination temperature increased. Similar trends can also be found elsewhere [37]. The lowest average size of anatase crystallite was estimated at 4.3 nm, which was prepared at 75 °C. As the calcination temperature increased to 200, 400, and 600 °C, the average crystallite size increased to 5.7, 9.4, and 49.4 nm, respectively. This result was evident from the XRD pattern, as in Fig. 1. It was observed that the width of the diffraction peak of anatase (101) at $2\theta = 25.4^\circ$ became narrower as the temperature increased from 75 °C to 400 °C. The same pattern of diffraction peak of TiO$_2$ rutile (110) at $2\theta = 27.5^\circ$ was also observed as the calcination temperature increased from 200 °C to 800 °C. Thus, it can be concluded that the crystallites sizes became reduced as the XRD peak got broader [38].

### 3.2. FTIR analysis

Fig. 2 shows the FTIR spectra of the synthesized TiO$_2$ at different calcination temperatures in the wavenumber range of 4000–650 cm$^{-1}$. It can be observed that all spectra exhibited two dominant absorption regions at 3000–3200 cm$^{-1}$ and at 1625 cm$^{-1}$ and 3400 cm$^{-1}$ except for T800. The broad peak located at 3100 cm$^{-1}$ was due to the stretching of $-\text{OH}$ group. A relatively sharp peak observed at 1625 cm$^{-1}$ was associated to –OH bending mode of water on the surface of TiO$_2$ [25]. It is interesting to note that there was a significant disappearance of peak at 3100 cm$^{-1}$ and 1625 cm$^{-1}$ with the elevation of the calcination temperature. T800 suffered both disappearances at 3100 cm$^{-1}$ and 1625 cm$^{-1}$ peaks while T600 only at 1625 cm$^{-1}$. In addition, it can be justified that the disappearance of these peaks was due to the loss of hydroxyl groups on the surface of TiO$_2$ as calcination temperature exceeding 600 °C was applied. Furthermore, the loss of hydroxyl groups contributes to the improvement in photocatalytic activity by their interactions with photogenerated holes, thus giving better charge transfer, which inhibits the recombination of electron–hole pairs [25,39]. The absorption at 1396 cm$^{-1}$ was due to $\text{C}–\text{H}$ stretching vibration corresponding to the residual organic species contaminant on the surface from alkoxide precursor [16,40]. Fig. 2 also shows the obvious peaks around 1346 cm$^{-1}$ and 1095 cm$^{-1}$ in T75, T200 and T400 samples due to the presence of N$_2$O$_2$ and $\text{NO}_x$ species [15,16,39]. In addition, those peaks are absent in the sample TAA and TP25. Therefore, the presence of these two peaks indicates that N$_2$O$_2$ and $\text{NO}_x$ species could be chemisorbed on the surface of the synthesized TiO$_2$. It can also be informed that N-doped TiO$_2$ can be prepared from this study. It was observed that the intensity of 1346 cm$^{-1}$ and 1095 cm$^{-1}$ peaks decreased as the calcination temperature increased. The complete disappearance of peak at 1346 cm$^{-1}$ can be seen in T800 sample. It might be due to the heat treatment up to 800 °C, in which it will decompose the N$_2$O$_2$ and $\text{NO}_x$ species and $\text{C}–\text{H}$ from residual organic contaminants. The small shoulder of 1095 cm$^{-1}$ peak assigned in the T800 spectra revealed small residues of $\text{NO}_x$ species on the surface of TiO$_2$.

### 3.3. Morphology analysis

Fig. 3 shows FESEM micrographs of N-doped TiO$_2$ anatase/rutile mixed phase nanorods assembled microspheres prepared by a simple and direct sol–gel method with HNO$_3$ as the nitrogen source at different calcination temperature 75 °C, 400 °C, and 600 °C. The morphologies in Fig. 3(a) and (b) indicate T75 sample (95% anatase and 5% rutile), while Fig. 3(c) and (d) indicate T400 sample (38.3% anatase and 61.7% rutile) and Fig. 3(e) and (f) indicate T600 sample (12% anatase and 88% rutile) with TiO$_2$ nanorods length of below 100 nm. The formation of TiO$_2$ microspheres as shown in Fig. 3(a), (c) and (e) was constructed by TiO$_2$ nanorods or rice-like structure as shown in Fig. 3(b), (d) and (f). It can be shown that the size of TiO$_2$ microspheres increased as calcination temperature increased. In addition, the increments in width of TiO$_2$ nanorods also observed as calcination temperature increased. This was due to the heat treatment which led to the aggregation of the TiO$_2$ nanorods building block and increased the size of these microspheres. Typical AFM images of T75 and T400 samples are shown in Fig. 4. The three-dimensional image in Fig. 4 reveals that prepared T75 and T400 samples showed regular spherical particles due to TiO$_2$ nanorod construction. The single formation of TiO$_2$

### Table 1

Crystalline properties of the TiO$_2$ nanorod prepared at different calcination temperature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Calcination temperature (°C)</th>
<th>Anatase (%)</th>
<th>Rutile (%)</th>
<th>BET surface area (m$^2$ g$^{-1}$)</th>
<th>Band gap (eV)</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T75</td>
<td>—</td>
<td>95.0</td>
<td>5.0</td>
<td>204.27</td>
<td>2.80</td>
<td>4.3</td>
</tr>
<tr>
<td>T200</td>
<td>200</td>
<td>52.8</td>
<td>47.2</td>
<td>200.73</td>
<td>2.54</td>
<td>5.7</td>
</tr>
<tr>
<td>T400</td>
<td>400</td>
<td>38.3</td>
<td>61.7</td>
<td>73.56</td>
<td>2.50</td>
<td>9.4</td>
</tr>
<tr>
<td>T600</td>
<td>600</td>
<td>12.0</td>
<td>88.0</td>
<td>27.95</td>
<td>2.60</td>
<td>49.4</td>
</tr>
<tr>
<td>T800</td>
<td>800</td>
<td>0</td>
<td>100</td>
<td>2.69</td>
<td>3.06</td>
<td>56.7</td>
</tr>
<tr>
<td>TAA</td>
<td>—</td>
<td>100</td>
<td>0</td>
<td>15.16</td>
<td>3.85</td>
<td>89.8</td>
</tr>
<tr>
<td>TP25</td>
<td>—</td>
<td>72</td>
<td>28</td>
<td>52.12</td>
<td>3.24</td>
<td>22.4</td>
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</tbody>
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Anatase Rutile Average

<table>
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<th></th>
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<th>Rutile</th>
<th>Average</th>
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<tbody>
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<td></td>
<td>4.3</td>
<td>5.7</td>
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<td></td>
<td>9.4</td>
<td>30.3</td>
<td>19.9</td>
</tr>
<tr>
<td></td>
<td>49.4</td>
<td>35.3</td>
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<td></td>
<td>22.4</td>
<td>31.0</td>
<td>26.7</td>
</tr>
</tbody>
</table>

Fig. 2. FTIR spectra of the synthesized TiO$_2$ at different calcination temperature.
microspheres assembled by TiO₂ nanorods can also be observed by TEM image as shown in Fig. 4(e) and (f). It is confirmed that the formation of this microsphere was constructed by TiO₂ nanorods with an average length of 70 nm and average width of 16 nm. These results were consistent with the XRD results.

The effect on size of morphological structure of the prepared TiO₂ powder before and after calcination was observed by using SEM. Fig. 5(a) shows very fine powder and small particle size. However, as shown in Fig. 5(b), the TiO₂ powder that was calcined at 800 °C exhibited severe aggregation phenomenon, which led to the formation of large TiO₂ particles and reduction in surface area. The same phenomenon can also be found elsewhere in previous studies [25,30,37]. The reduction in surface area was proven by the BET analysis, as shown in Table 1. It indicated that TiO₂ calcined at 800 °C exhibited the lowest surface area of 2.69 m² g⁻¹. Meanwhile, the TiO₂ dried at 75 °C revealed the highest surface area of 204.27 m² g⁻¹ as compared to TAA and TP25 with surface area of 15.16 m² g⁻¹ and 52.12 m² g⁻¹ respectively.

3.4. UV–Vis spectroscopy

In order to study the effect of calcination temperature on the optical response of the prepared TiO₂, an analysis using UV-NIR spectrophotometer was performed. The UV–Vis spectra of TiO₂ powder prepared at different calcination temperatures are illustrated in Fig. 6. It is indicated that all of the prepared TiO₂ exhibited excellent optical responses to UV and visible regions, especially T600 sample. Different optical responses were observed in this study as compared to previous studies [18,26,27,41–44] as a different approach was implemented. In contrast, dopant materials were introduced in previous studies for the preparation of visible light active photocatalyst such as multi-walled carbon nanotubes (MWCNTs), sulphur, natural dyes, vanadium, and nitrogen. In the present study, almost all the TiO₂ samples prepared can be activated in visible light, which might be ascribed to the N-doping during the preparation step using HNO₃ as a catalyst [45]. Fig. 5 shows that as calcination temperature increased up to 600 °C, the absorption of synthesized TiO₂ in visible region increased gradually. Consequently, it can absorb higher fraction of photons from visible region [11]. In addition, as the calcination temperature increased up to 800 °C, a reduction of absorption in visible region was observed. Possible explanation for this reduction has a direct relation with crystallite phase transition and loss of specific surface area [25,37,46]. It had been proven from the XRD analysis; that a complete phase transition from anatase to rutile occurred at 800 °C as shown in Fig. 1. Furthermore, it might also be due to loss of N₂O₂⁻².
Fig. 4. Typical atomic force microscope images of (a), (b) T75 and (c), (d) T400. (a), (c) is 3D view and (b), (d) is height view. (e), (f) is TEM image of the TiO$_2$ microsphere assembled TiO$_2$ nanorods for sample T400.

Fig. 5. The effect on size of morphological structure of the prepared N-doped TiO$_2$ powder before and after calcination: (a) T75 and (b) T800.
species as shown in Fig. 2. The loss of N$_2$O$_2^{2-}$ species will limit the incorporation of nitrogen in TiO$_2$ lattice and lower the optical responses in visible light [9,14,39,47]. The substituted nitrogen atoms in the doped TiO$_2$ lattice have been completely substituted by oxygen atoms with increasing calcination temperature [48].

The strong absorbance in UV region of all the TiO$_2$ samples was due to the high tendency of electron excitation from the valence band to the conduction band. T600 sample, which consisted of 12% anatase and 88% rutile, exhibited the highest absorbance in the visible region, followed by T800, T400, T200, and T75. From the spectrum, it could be observed that there were absorbance differences in the UV light and visible regions between the samples. The sample calcined at 800 °C showed a relatively low absorbance rate in the UV region due to the increase in particle size. Previous studies have suggested that this may be attributed to the combined effects of particles size and crystallinity [25,37]. A lower absorbance rate at the UV range led to low responses towards UV light. It can be concluded that as the particles are low in crystallinity and large in particle size, the tendency to absorb UV light is limited, which is due to the smaller surface in the limit areas [25].

The increment in calcination temperature led to this aggregation phenomenon as shown in Fig. 3, as it turned out to be more severe and corresponded roughly to the result of UV/Vis spectrum, whereby the UV responses of the samples decreased as the calcination temperature increased. Thus, calcination temperature at 600 °C is considered as the optimum condition for preparing N-doped TiO$_2$ with the highest absorption capacity under visible region.

From spectra in Fig. 6, the band gap energy of prepared TiO$_2$ was estimated according to $(\alpha \nu v) = A(\nu v - E_g)^2$, where $A$ is constant, $\nu$ the photon energy, $E_g$ is optical band gap [36]. The $\nu$ was derived from $\nu = h c / \lambda$, where $h$ is plank constant (4.136 × 10$^{-15}$ eV), $c$ is the light velocity in vacuum (2.977 × 10$^{17}$ nm/s), and $\lambda$ is the wavelength (nm). The band gap energies of the investigated N-doped TiO$_2$ are summarized in Table 1. The obtained band gap energies for T75, T200, T400, T600, and T800 are found to be 2.93, 2.81, 2.80, 2.83, and 3.08 eV respectively which are lower than TP25 and TAA. The band narrowing arises from the contributions of nitrogen atoms presence in the TiO$_2$ lattice structure which induce the local states above the valence band edge and the oxygen vacancies give rise to the local states containing of the 3d states of Ti$^{3+}$ below the conduction band edge [12]. Furthermore, anatase to rutile transformation is accompanied by the growth of rutile crystallite size, the mixed phase TiO$_2$ possesses a mixture of band gap configuration [10]. Therefore, the band gap energies of prepared TiO$_2$ anatase/rutile mixed phase is reduce might be due to increasing of rutile phase since the band gap of pure anatase (3.2 eV) is larger than that (3.0 eV) of pure rutile TiO$_2$ [49]. The results suggesting a considerably narrower band gap which suitable for the photocatalytic activity under visible light irradiations as compared to the TP25 and TAA.

3.5. X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy analysis was performed to study the present of nitrogen doping concentration in TiO$_2$ lattice structure. The range of the binding energy from 404 to 394 eV corresponds to the peak of N 1s spectra are shown in Fig. 7. The binding energies of N 1s for sample T400 was detected at 396.8, 397.5, 398.7, and 399.8 eV while for sample T600 was detected at 401 eV. Previous studies suggested that the N 1s peak of the N-doped TiO$_2$ was commonly observed between 395 and 402 eV [16,36,48,50–53]. The existence of the binding energy at 396.8, 397.5, 398.7, and 399.8 eV has confirmed the success of the N-doping in the TiO$_2$ lattice structure. The peak at 396.8 eV is attributed to the Ti–N bonds in TiO$_2$ [14]. Previous studies reported that the binding energy at 397.5 eV is indicative of N atom replacing oxygen in the TiO$_2$ crystal lattice and the formation of N–Ti–N bond [54–56]. The N 1s peak of the prepared TiO$_2$ at 399.8 eV can be attributed to interstitial nitrogen species or the presence of
oxidized nitrogen similar to NOx species which the possibility of N—O—Ti or Ti—N—O bond formed on the TiO2 crystal surface [57–59]. The N 1s peak at 401 eV in sample T600 can be attributed to oxidized nitrogen, such as Ti—O—N or Ti—N—O linkages in N—TiO2, which may come from the interstitialal N [12]. From XPS analysis, the concentration of the nitrogen in the TiO2 crystal lattice is about 1.5% (atomic percent) and 1.1% (atomic percent) for sample T400 and T600 respectively. These result indicated that the at high calcination temperature, the concentration of the nitrogen in the TiO2 is decreased as described in FTIR analysis. It have been concluded that, at lower doping levels (<2.1% atomic percent) that the substitution of N atom in TiO2 crystal lattice will introduce localized N 2p states above the valence band which improves the absorption capability under visible light irradiation [60]. The results showed that the concentration of the nitrogen in the prepared sample is varied as compared to the previous study. It might be due to the sample preparation techniques and nitrogen sources [16,54,61].

3.6. Photocatalytic activity measurements

The degradation of phenol in aqueous solution under UV and visible light irradiations was investigated in order to examine the photocatalytic activity of N-doped TiO2 nanorods. Fig. 8(a) and (b) show the degradation of phenol in the presence of 0.4 g of the produced N-doped TiO2 nanorods prepared at different calcination temperatures (T75, T200, T400, T600, and T800) for UV and visible light irradiations respectively. The adsorption of phenol on the surface of TiO2 samples were found to be 15%, 13.5%, 12%, 4%, 3.03%, 2.4% and 0.1% for T75, T200, T400, T600, T800, TP25, and TAA respectively after 1 h under dark condition. Commercial TiO2 (TAA & TP25) was used in this experiment for comparison purpose. The blank experiment was conducted in order to study the stability of phenol by direct photolysis under UV and visible light irradiations without the presence of photocatalyst. It can be observed that there was no significant reduction in initial concentration of phenol after having been irradiated under UV (312 nm) and visible light (>420 nm) for 540 min, as shown in Fig. 8. The direct photolysis showed the lowest degradation of phenol in aqueous solution, with only 2.04% and 0% degradation under UV and visible light irradiations respectively. It is confirmed that phenol will not be degraded by visible light irradiation [50]. However, it could be seen that the concentration of phenol in aqueous solution decreased upon UV and visible light irradiations for 540 min with the presence of photocatalyst. All synthesized N-doped anatase/rutile mixed phase TiO2 nanorods calcined at different calcination temperatures were able to degrade phenol under UV and visible light. In contrast, TAA and TP25 could only degrade phenol under UV light irradiation. It is well known that TAA and TP25 suffer large band gap which can only be activated upon irradiation with photons of light in the UV region (λ ≤ 387 nm), which limits the photocatalytic activity under visible light irradiation [9].

The summary of the photocatalytic activity for all prepared photocatalysts for the degradation of phenol after 540 min is presented in Table 2. It was clearly observed that the highest photocatalytic activity was obtained using T400 sample, which was higher than commercial TiO2 (TAA and TP25). The performance of this catalyst has been proven in previous studies where the anatase/rutile mixed phase TiO2 exhibit higher photocatalytic activity than the single phase anatase and rutile TiO2 under UV light irradiation [8,30,62–64]. The highest photocatalytic activity in the anatase/rutile mixed phase TiO2 might be attributed to the electron affinity within the anatase and rutile phases. It has been proven that the electron affinity of anatase is higher than rutile [65]. The rapid photogenerated conduction electron flows from anatase to rutile, and thus, limits the electron recombination rate [8]. It is well known that the conduction band potential of rutile is more positive than that of anatase, which means that the rutile phase may act as an electron sink for photogenerated electrons from the conduction band of the anatase phase [9]. A previous study on the band alignment of rutile and anatase TiO2 indicated that the band alignment of approximately 0.4 eV drive force for the increased the photocatalytic activity of anatase/rutile composites material over their individual counterparts [4].

The differences in photocatalytic activity of T75, T200, T400, T600, T800, TAA and TP25 are most likely dependent on the capability of light response, phase composition, surface area, size, crystallinity, effect of N-doping, and number of active sites. As tabulated in Table 2, it was revealed that the prepared N-doped anatase/rutile mixed phase TiO2 nanorods exhibited the highest photocatalytic activity in both UV and visible regions than in TAA, TP25, and T800. As shown in Fig. 8(a) and (b), T400 showed the
highest photocatalytic activity of 99.60% and 99.16% of phenol degradation, which had been achieved after being irradiated under UV and visible light for 540 min respectively. Besides, TAA and TP25 exhibited the lowest photocatalytic activity under visible light irradiation due to its capability that was limited in visible regions since there was no N doped in TiO2 lattice. Notably, T75, T200, T400 and T600 exhibited higher photocatalytic activity under visible region due to the ability to absorb photon from the visible region. The introduction of N-doped in the TiO2 lattice increased the visible light activity dramatically [11].

Calcination temperature plays an important role in the preparation of photocatalyst for photocatalytic process. The highest photocatalytic activity under both UV and visible light might be related to the crystalline properties of the TiO2 nanorods, which include being well crystallized, appropriate phase composition, significantly small particles, high surface area (refer Table 1) and the presence of superficial hydroxyl group. However, for the photocatalyst calcined above 600 °C, the decline in photocatalytic activity was observed under both UV and visible light. Therefore, T800 exhibited the lowest photocatalytic activity among calcined samples under UV and visible light of 44.88% and 52.99% of phenol degradation for 540 min of irradiation time respectively. This was due to the calcination temperature up to 800 °C having complete transformed anatase to rutile phase, thus limiting its photocatalytic activity. Furthermore, as calcination temperature increased up to 800 °C, TiO2 suffered severe aggregation phenomenon, which led to the formation of large TiO2 particles. Hence, a low surface area was created for the photodegradation reaction to take place. A low optical response to UV leads to insufficient energy to excite electron from valence band to the conduction band [6]. The excitation of electron is crucial since it leads to the formation of positive holes and has a positive charge [66]. This positive hole has strong oxidation power to promote the degradation of phenol molecules in aqueous solution.

4. Conclusions

N-doped TiO2 anatase/rutile nanorods assembled microsphere was successfully prepared using titanium-n-butoxide Ti(OBu)4, nitric acid, and isopropanol as a precursor material, catalyst and solvent, respectively. The preparation of N-Doped TiO2 anatase/rutile nanorods assembled microsphere with controllable heating treatment is a very simple and energy saving approach. This study has shown the effects of calcination temperature on the physico-chemical properties and photocatalytic activity. The results showed that the calcination temperature plays an important role in the crystallites growth and the crystallites phase transition in the preparation of the highly active photocatalyst. Based on the XRD pattern, it can be concluded that the increment in calcination temperature leads to rapid crystallite growth and a decrease in particle size. Furthermore, the composition of anatase will decreased while the composition of rutile increased in N-Doped TiO2 anatase/rutile nanorods assembled microsphere as the calcination temperature increased. BET analysis revealed a decrease in the TiO2 surface area, which was also due to the elevated calcination temperature. From the UV–Vis spectra, all the TiO2 samples prepared in the laboratory exhibited excellent optical responses under UV and visible regions. The highest photocatalytic activity both under UV and visible regions was demonstrated by the N-Doped TiO2 anatase/rutile nanorods assembled microsphere prepared at 400 °C of calcination temperature. The degradation of approximately 99% was achieved after 540 min of irradiation time. Apart from that, the differences in photocatalytic activity were most likely dependent on the capability of light response, phase composition, surface area, size, crystallinity, effect of N-doping, and number of active sites. N-doped TiO2 anatase/rutile nanorods assembled microsphere as prepared in this study can be used as an appropriate photocatalyst material with effective performance in a broader range of light spectrum i.e., from UV to visible light in phenol degradation applications.

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