

N-doped TiO₂ Synthesised via Microwave Induced Photocatalytic on RR4 Dye Removal under LED Light Irradiation

(TiO₂ Terdop N Disintesis melalui Ketuhar Gelombang Mikro Teraruh kepada Fotopemangkinan terhadap Penyingkiran Pewarna RR4 di bawah Sinaran Cahaya LED)

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ABSTRACT

Nitrogen doped titanium dioxide (N-doped TiO₂) was synthesized by microwave using urea as nitrogen sources with commercially available TiO₂-P25. The N-doped TiO₂ was compared with unmodified TiO₂ by carrying out the investigation on its properties using x-ray diffraction (XRD) analysis, Brunauer-Emmett-Teller (BET), Fourier transformed infrared spectroscopy (FTIR) and diffuse reflectance spectroscopy (UV-Vis DRS). The photocatalytic activities of N-doped TiO₂ and unmodified TiO₂ were studied for photodegradation of reactive red 4 (RR4) under light emitting diode (LED) light irradiation. An active photoresponse under LED light irradiation was observed from N-doped TiO₂ with 60 min of time irradiation to complete RR4 color removal while no photocatalytic degradation was observed from unmodified.

Keywords: Dye light emitting diode; microwave; nitrogen doping; photocatalysis; reactive red 4

ABSTRAK

Titanium dioksida terdop nitrogen (TiO₂ terdop N) telah disintesis oleh ketuhar gelombang mikro menggunakan urea sebagai sumber nitrogen dengan TiO₂-P25 yang boleh didapati secara komersial. TiO₂ terdop N telah dibandingkan dengan TiO₂ tidak diubah suai dengan menjalankan kajian ke atas sifatnya menggunakan analisis pembelauan sinar x (XRD), Brunauer-Emmett-Teller (BET), spektroskopi transformasi Fourier inframerah (FTIR) dan spektroskopi pantulan meresap (UV-Vis DRS). Aktiviti fotopemangkinan TiO₂ terdop N dan TiO₂ tidak diubah suai telah dikaji untuk pemfotorosotaan reaktif merah 4 (RR4) di bawah sinaran cahaya LED. Tindak balas foto aktif di bawah sinaran cahaya LED diperhatikan daripada TiO₂ terdop N dengan 60 min masa penyinaran untuk melengkapkan penyingkiran warna RR4 manakala tiada kemusnahan fotopemangkinan diperhatikan daripada TiO₂ tidak diubah suai.

Kata kunci: Diod pemancar cahaya; fotopemangkinan; ketuhar gelombang mikro; pendopan nitrogen; reaktif merah 4 pewarna

INTRODUCTION

Heterogeneous photocatalysis has gained much attention toward the degradation of water pollution since this photocatalyst can achieve a complete mineralization in photocatalysis degradation process of organic pollutants. Heterogeneous photocatalysis is the process basically based on generates the hydroxyl radical which is highly oxidizing agents (Gaya & Abdullah 2008). This hydroxyl radical will oxidize the organic pollutants into harmless products. The combination between semiconductor photocatalyst and light sources is the key process of photodegradation. Titanium dioxide (TiO₂) is one among the semiconductor materials that widely used by researchers due to the chemically stable, low cost, non-toxic, reusable and its high photocatalytic activity (Nawi & Sheilatina 2012; Tseng et al. 2010). However, this material consists of wide band gaps between 3.0 and 3.2 eV which require only UV light irradiation to utilize the activation. Thus, the limit of their photocatalysis process since UV light consist only 3% from sunlight (Castillo-Ledezma & Sa´nchez Salas 2011; Cong et al. 2007).

Visible light irradiation is the main composition from sunlight. The modification of TiO₂ photocatalyst towards visible active catalyst is has been tremendously exploited since 1972 where the first discovery of TiO₂ on its capability to produce hydroxyl radical under activation of UV light (Hashimoto et al. 2005). Some researchers made a modification of TiO₂ by using the doping technique with metal and nonmetal element (Kuo et al. 2011; Wodka et al. 2010; Yu et al. 2014). Some researchers claimed that doping with metal may decrease the band gap energy. However, metal doped can also act as a recombination center of electron and holes thus, reducing the photocatalytic activity (Larumbe et al. 2015; Meng et al. 2007). Some of the nonmetal doping TiO₂ have been explored such as nitrogen (Hou et al. 2014; Ilinoiu et al. 2013; Michael et al. 2014), carbon (Park et al. 2009; Wu et al. 2013), sulphur (Liu & Chen 2008; Rengifo-Herrera et al. 2009), boron (Ochiai et al. 2010) and phosphorus (Xia et al. 2014; Zheng et al. 2010). These nonmetal elements exhibit red-shifted absorption edges. In previous works indicated that N doping supreme potential toward

the visible-light absorption due to the metastable center formation, small ionization energy and its comparable atomic size in oxygen (Pelaez et al. 2012; Shin et al. 2015). Various procedures are already done with the intention of preparation N-doped TiO₂ such as solvothermal, ion implantation, sol-gel, calcination, sonochemical and sputtering techniques (Bangkedphol et al. 2010; Chen et al. 2007; Wang & Lim 2010). Conversely, these previous methods are very complicated due to the process either using specific equipment for modification or involved lots of chemical like a solvent to dissolve the precursor (Kim et al. 2013).

The main purpose of this study was to synthesize using commercially available TiO₂ (P25) assisted by microwave which is to produce visible light active N-doped TiO₂ by using urea as N precursor. A heating under microwave is well discovered that can accelerate the preparation time as well as less energy consumption. The photocatalytic activities under LED light irradiation were tested by photodegradation of anionic RR4 dye as a model pollutant.

MATERIALS AND METHODS

MATERIALS REQUIRED

TiO₂ Degussa P25 powder was used as the starting material in the preparation N-doped TiO₂. Urea from Fluka (chemical formula: NH₂CONH₂, molecular weight: 60.06 g mol⁻¹) was used as the N precursor. Reactive red (RR4) dye or commonly known as Cibacron Brilliant Red (Colour Index Number: 18105, chemical formula: C₃₂H₂₃ClN₈Na₄O₁₄S₄, molecular weight: 995.23 g mol⁻¹, λ max: 517 nm). Ultra-pure water was used to prepare all solutions in this work.

CATALYSTS SYNTHESIS AND CHARACTERIZATION

TiO₂ Degussa P25 was synthesized by mechanical mixing using weight ratio TiO₂: Urea = 7:3 for 5 min in the ball mill. The mixed powder was placed into a conical flask in the semi-closed reactor and heated by using the microwave at the power irradiation 800 Watt for 30 min under normal atmospheric condition. The sample was cooled down to the room temperature and the yellow light powder was denoted as N-doped TiO₂.

The crystalline structure of the photocatalyst was investigated using XRD analysis (Rigaku, Miniflex II Desktop X-Ray Diffractometer). Brunauer-Emmett-Teller (BET) was used to investigate the surface area of the photocatalyst. The band gap energy of photocatalyst was determined by using UV-Vis spectrophotometer, model Lambda 35 from Perkin Elmer equipped with diffuse reflectance attachment at the wavelength of 200-800 nm. Fourier-transform infrared spectroscopy (FT-IR) analyses were conducted to investigate the functional group contain in the photocatalyst were recorded in the 4000 to 1000 cm⁻¹ region. X-ray photoelectron spectroscopy (XPS) measurement was used to detect the presence of nitrogen

binding on the titania that is responsible for the visible absorption.

ADSORPTION STUDY

For adsorption study, the sample was conducted in the dark. In each test, 0.030 g of photocatalyst samples was added into a 25 mL of 30 mg L⁻¹ anionic RR4 dye to form suspensions. This suspension was poured into a glass cell with dimension 50 × 10 × 80 mm (L × B × H) and aerated in the dark. An aquarium pump model NS 7200 was used as the aeration source. The decolorization degree of RR4 was determined at specific time interval until complete decolorization was achieved. The absorbance was measured by using HACH DR 1900 spectrophotometer at 517 nm. All experiments data were collected based on three repetitions.

EVALUATION OF PHOTOCATALYTIC ACTIVITY

The photocatalytic performances of the N-doped TiO₂ and unmodified TiO₂ samples were investigated in the degradation of RR4 dye under LED light irradiation. The photodegradation activity was carried out by adding 0.030 g of photocatalyst sample into 25 mL of 30 mg L⁻¹ RR4 dye to form suspensions. This suspension was then poured into a glass cell with dimension 50 × 10 × 80 mm (L × B × H) and irradiated with 20 Watt LED lamp with light intensity (Visible: 237 W m⁻²) was used as the visible light source. An aquarium pump model NS 7200 was used as an aeration source for oxygen supply. During each photocatalytic experiment, the decolorization degree of RR4 was determined at specific time interval until complete decolorization was achieved. The absorbance was measured by using HACH DR 1900 spectrophotometer at 517 nm. All experiments data were collected based on three repetitions.

RESULTS AND DISCUSSION

CHARACTERIZATION STUDY OF PHOTOCATALYST

The X-ray diffraction (XRD) patterns of N-doped TiO₂ were presented on Figure 1, where A stand for Anatase and R stand for Rutile. The XRD pattern of N-doped TiO₂ in Figure 1 shows a diffraction signal at 25.28°, 37.91°, 41.37°, 48.12°, 53.96°, 55.25°, 62.97°, 70.55°, 75.28° and 82.95°, this signal assign to the characteristic signal of anatase. Simultaneously, another signal showed the XRD pattern which is at 27.38°, 36.02°, 41.18°, which assign as rutile signal in N-doped TiO₂. The two different phases appeared due to the mixture of two type of TiO₂ which is anatase and rutile also known as P25 (70% anatase and 30% rutile). The crystal structure of N-doped TiO₂ and unmodified TiO₂ shows similar pattern even the modified TiO₂ was already synthesised under microwave irradiation. Hence, we can claim that the synthesis using microwave irradiation does not affect the crystal structure that consist anatase and rutile in unmodified TiO₂ (P25).

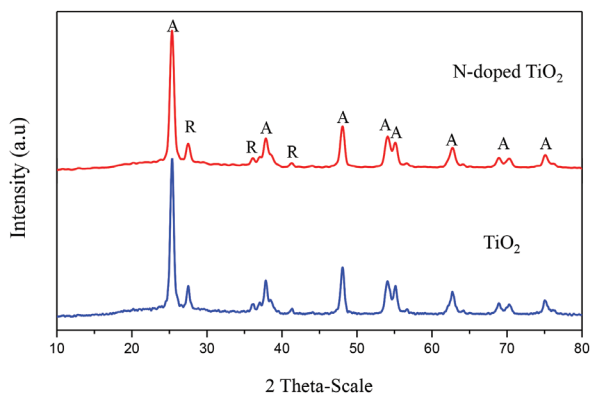


FIGURE 1. XRD patterns of N-doped TiO₂ and unmodified TiO₂

BET analysis was carried out to investigate the specific surface area (SSA) of the samples. The surface area from BET analysis of unmodified TiO₂ and N-doped TiO₂ are listed in Table 1. The surface area of N-doped TiO₂ sample shows a slight decreasing value compared to unmodified TiO₂ by 14%. This phenomenon is due to the sintering effect produced from rapid heating of microwave irradiation that reduces the pore size of N-doped TiO₂ and eventually reducing the surface area of the sample. The Fourier transform infrared (FT-IR) spectrum of unmodified TiO₂ and N-doped TiO₂ was studied to confirm there is functional group shows the bonded between nitrogen and TiO₂. Nitrogen bonded will enhance the photocatalytic activity under visible light region. FT-IR spectra of N-doped TiO₂, unmodified TiO₂ and urea samples were as shown in Figure 2.

The spectrum shows the different peak was created by N-doped TiO₂ comparing with unmodified TiO₂. The spectrum

of N-doped TiO₂ give several strong at the region 1400-1643 cm⁻¹ meanwhile unmodified TiO₂ a peak at 1638 cm⁻¹ representative of adsorbed H₂O was the only peak in the same region (Nicholas et al. 2011). As can be seen on the figure, the N-doped TiO₂ displays the typical features of urea corresponding to N-H on the peaks of 3150-3600 cm⁻¹ and 1600-1650 (Factorovic et al. 2011). The small peak appeared at 1449 cm⁻¹ was detected as -N-O_x (Huang et al. 2008). No C=O bond was detected in N-doped TiO₂ representing the element in urea. Thus, FTIR spectrum is proved that urea was completely decomposed under microwave producing N-O and N-H bond incorporated with TiO₂ to form N-doped TiO₂.

X-ray photoelectron spectroscopy (XPS) measurements were carried out to detect the chemical state and composition of the N-doped TiO₂ at the surface species. Figure 3(a) and 3(b) displays the XPS spectra of N 1s and O 1s for the N-doped TiO₂ sample, respectively. From Figure 3(a), it is clearly shown that the N 1s spectra with deconvolution peaks detected at 400.3 and 404.8 eV representing interstitial N in the form of N-O bond. However, a few reported on N 1s peak above 400 eV assigned as chemisorbed nitrogen, NH₃ adsorbed on the surface TiO₂ and trapped N₂ gas (Sathish et al. 2007; Yates et al. 2006) but, many works have agreed and pointed out that the binding energy at 400 eV and above is assigned as interstitial N-O species (Hu et al. 2012; Lin et al. 2013; Zhu et al. 2010). Peak at 404.8 eV of N 1s represented as surface adsorbed nitrogen species which is the nitrogen species bound to various surface oxygen site such as NO, NO₂ or NO_x (Etacheri et al. 2012). Sathish et al. (2005) discovered that although the deconvolution N 1s at the peak 400 eV is not being prove experimentally but hypothesized that the bonding energy of N 1s is higher when the nitrogen atom

TABLE 1. Surface area and band gap energy of unmodified TiO₂ and N-doped TiO₂

Samples	S _{BET} (m ² g ⁻¹)	E _{bg} (eV)
TiO ₂	49.0	3.02
N-doped TiO ₂	44.0	2.9

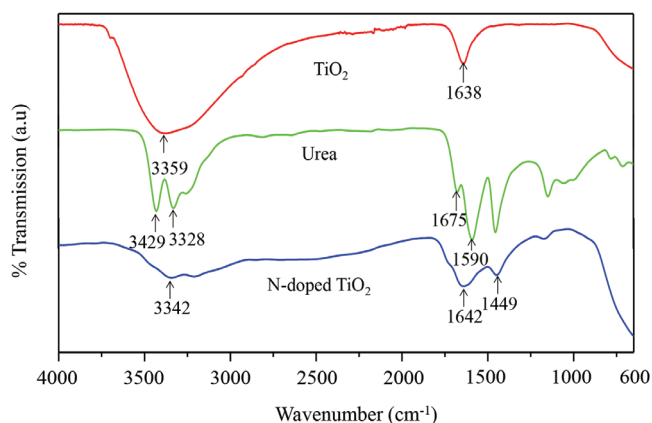


FIGURE 2. FTIR spectrum of N-doped TiO₂, unmodified TiO₂ and urea

in a chemically linkage shows more positive formal charge. Consequently, N 1s binding energy at the peak 400.3 eV for N doped TiO₂ sample in this study can be attributed to the formation of interstitial N and directly bounded to lattice oxygen. The XPS spectra of the O 1s core level consist one the major peak at 531.3-531.5 eV was detected in N-doped TiO₂ as shown in Figure 3(b). The formation of hyponitrite (N₂O₂)⁻² was assigned at the peak 531.5 eV which it was caused by the N interstitially doping into the lattice TiO₂ (Hu et al. 2012; Peng et al. 2008).

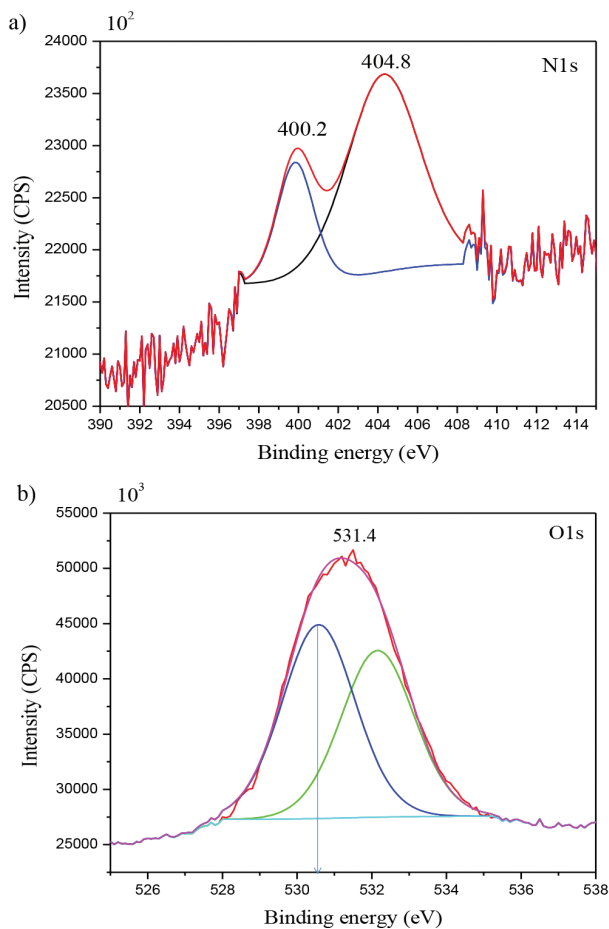


FIGURE 3. XPS spectra of N-doped TiO₂ sample; (a) N 1s and (b) O 1s

The presence of nitrogen in TiO₂ will narrow the band gap of TiO₂. Thus, the UV-Vis DRS analysis will prove there is narrowing band gap in the TiO₂. Figure 4(a) and 4(b) shows the UV-Vis diffuse reflectance spectra and plot graph Kubelka-Munk versus energy eV for samples N-doped TiO₂ and unmodified TiO₂. Based on Figure 4(a), the absorption edge of unmodified TiO₂ is around 400 nm while for N-doped TiO₂ is around 430 nm. A wavelength for UV light is from 200 to 400 nm while wavelength for visible light is from 401 to 700 nm (Alexei et al. 2008). N-doped TiO₂ sample shows the shifted absorption towards visible light region while unmodified TiO₂ in the UV region. This

observation shows that N atom in urea was significantly reacted with TiO₂ particles producing defect structure thus, narrowing bandgap energy of photocatalyst. Figure 4(b) shows plot graph Kubelka-Munk versus energy eV to determine band gap energy of unmodified and N-doped TiO₂. The band gap energy was determined by Tauc's equation as stated in (1):

$$(\alpha hv) = (hv - E_g)^n, \quad (1)$$

where α is the absorption coefficient; $h\nu$ is the photo energy; n is a constant accounting for the type of optical transition; and E_g is the absorption band gap energy. Since Kubelka-Munk ratio is a function of reflectance, it is reciprocally used $F(R)$ (Tauc & Menth 1972). Assuming remarkably effective absorption then $\alpha = F(R)$. The Tauc band gap can be attained through intercept the plot of $(F(R)h\nu)^{1/n}$ against $h\nu$ (eV). Band gap energy for sample can be measured by extrapolation of the slope on graph until x -axis,

$$(F(R)h\nu)^{1/n} = (h\nu - E_g). \quad (2)$$

Based on extrapolation samples on Tauc bandgap graph in Figure 4(b), bandgap energy for unmodified TiO₂ was measured around 3.02 eV while the band gap for N-doped TiO₂ is around 2.9 eV. It is clearly shown that band gap energy value for N-doped TiO₂ is getting lower by comparing with unmodified TiO₂ thus, it clearly shows that N atom in urea was significantly reacted with TiO₂ particles producing defect structure as previously explained. This observation is in line with other researchers, according to Feng et al. (2008) they reported the narrowing of band gap energy was due to the introducing of the impurity level between the valence and conduction band of TiO₂. Nawawi and Nawi (2013) also reported the narrowing band gap is associated with the doped of N presence in modified photocatalyst.

ADSORPTION STUDY

In this study, anionic RR4 dye was used to determine the adsorption study of N-doped TiO₂. Based on Figure 5, it shows that both unmodified TiO₂ and N-doped TiO₂ were managed to adsorb almost 50% of 30 mg L⁻¹ RR4 dye with adsorption of N-doped TiO₂ shows a better result than unmodified TiO₂. Higher adsorption rate is related to the high specific surface area which attracted more dye substrates to its surface (Nawawi & Nawi 2013; Wang et al. 2015). The degradation of organic pollutants by TiO₂ photocatalyst occurs primarily on or near the surface of the catalyst and thus, adsorption is a critical factor in the efficiency of the process. Larger specific surface area means more adsorption sites. Sample with the larger specific surface area can pre-adsorb more dye molecules on the surface of the sample. From our finding, the results showed different where unmodified TiO₂ with highest

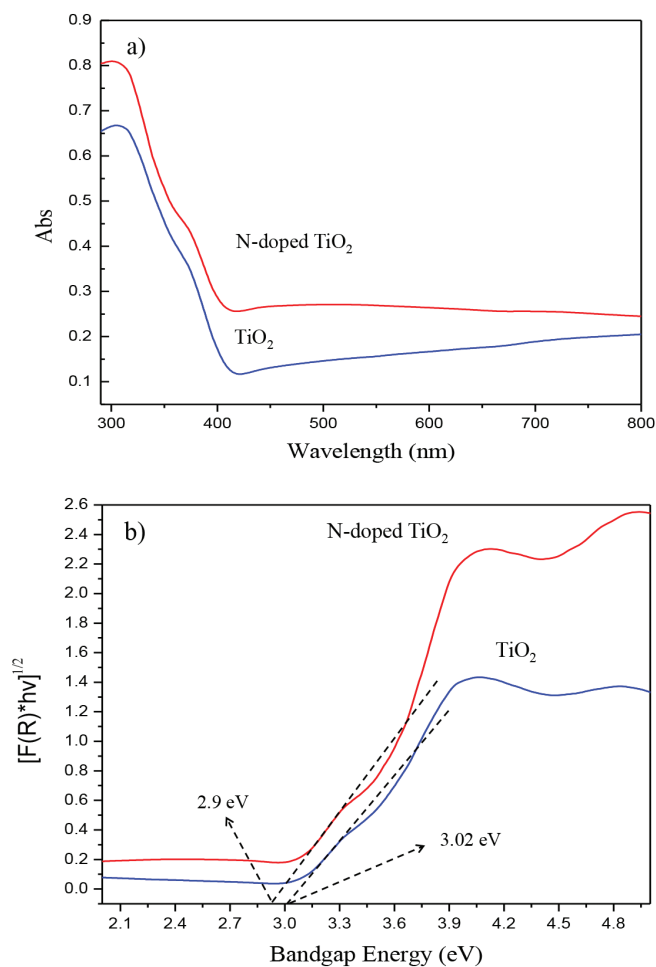


FIGURE 4. a) Graph UV-VIS DRS of TiO₂ and N-doped TiO₂ and b) graph Kubelka-Munk vs. bandgap energy of TiO₂ and N-doped TiO₂

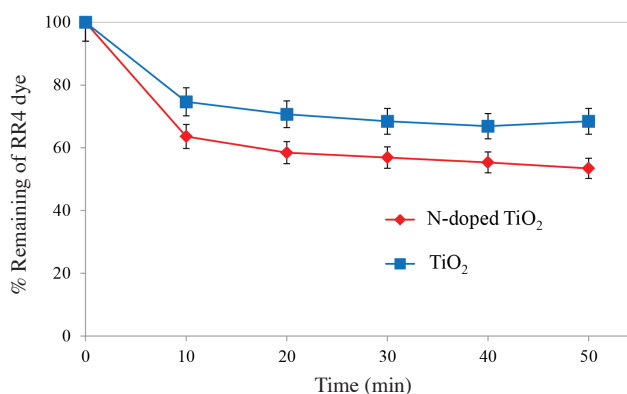


FIGURE 5. The adsorption study of unmodified and N-doped TiO₂ under 30 mg L⁻¹ RR4 dye, (STDVE range: 3-4)

surface area shows a slightly lower of its adsorption by 10% compare with N-doped TiO₂ (Table 1). This is due to the coulombic attraction by the positively charged of unmodified TiO₂ and N-doped TiO₂ proven by measuring of these photocatalysts using zeta potential at ambient

condition (pH5.5). The zeta potential value of unmodified TiO₂ was measured about 0.79 mV while the zeta potential for N-doped TiO₂ was 15.57 mV and this explained adsorption of RR4 under N-doped TiO₂ was higher than unmodified TiO₂.

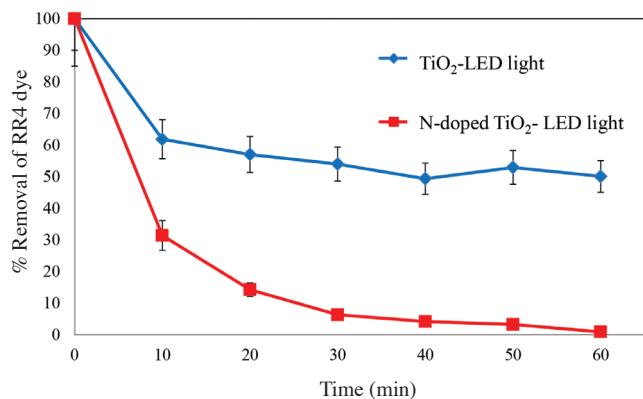


FIGURE 6. Photocatalytic degradation of unmodified and N-doped TiO₂ under LED light irradiation, (STDVE range: 4-8)

PHOTOCATALYTIC PERFORMANCE

Figure 6 shows the photocatalytic degradation of RR4 dye by N-doped TiO₂ and unmodified TiO₂ under LED light (Vis: 237 W m⁻², UV: 0 W m⁻²). It was found that N-doped TiO₂ only took only 60 min to complete the degradation of RR4. No photocatalytic degradation under unmodified TiO₂ was observed. However, RR4 dye was removed about 40% for 30 min and no decreasing was detected after prolonging the irradiation. The percentage of RR4 removal under unmodified TiO₂ was due to the adsorption of TiO₂ particle since the same trend observed on unmodified TiO₂ under both adsorption and visible light conditions as can be seen in Figures 5 and 6, respectively. N-doped TiO₂ contributed the positive result when it was active under visible light irradiation. Thus, it clearly proved that the N element in TiO₂ reduced the band gap energy of N-doped TiO₂ makes N-doped TiO₂ active under the low energy of visible light.

CONCLUSION

A simple technique was successfully applied for the preparation of visible light active N-doped TiO₂ by mixing urea and TiO₂ powder under microwave irradiation. The FTIR spectrum was confirmed that the nitrogen was successfully bonded into TiO₂ surface and there is no change in the crystalline structure of N-doped TiO₂ after synthesized under microwave irradiation. The XPS analysis was chemically identified that the nitrogen incorporated with titania crystal to producing Ti-O-N linkage. BET analysis shows the N-doped TiO₂ produce low surface area compared with unmodified TiO₂. The band gap energy of the N-doped TiO₂ was reduced to 2.9 eV recorded by UV-Vis DRS spectrum. In addition, the presence of N-doped makes N-doped TiO₂ active under visible light irradiation.

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