

PREPARATION OF N-TiO₂ PHOTOCATALYTIC SYNTHESIZED BY SOL-GEL METHOD FOR INHIBITIVE FORMATION OF CARCINOGEN IN FOODS

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Abstract

The photocatalytic for inhibitive formation of carcinogen in potassium nitrate solution by using visible light was investigated in this research. N-doped TiO₂ (N-TiO₂) powder was prepared by sol-gel method. Titanium (IV) butoxide was used as the precursor, Ammonium nitrate as the nitrogen source. The obtained gel were calcined with various conditions to investigate the optimum calcined temperature and time in order to obtain N-doped TiO₂ powder. Photocatalytic samples were prepared by dipping N-TiO₂ slip on sponges substrate. The synthesized powder were characterized by means of X-ray diffraction (XRD), Transmission electron microscope (TEM), Ion chromatography (IC) and specific surface area by BET. The results of X-ray diffraction patterns showed the ammonium nitrate was completely decomposed and obtained single phase of anatase which formed at the calcining temperature of 300°C for 60 min. The particles size were uniformly distributed with the average of 20 nm confirmed by transmission electron microscope (TEM). An optimum condition of N-TiO₂ synthesized powder can be removed nitrate 65.63%.

Keywords: N-doped TiO₂, sol-gel method, photocatalyst, TiO₂, calcination

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Introduction

Recently, cancer is becoming a significant health problem. Several factors are the leading cause of cancer risk, for example, chemical, ultra violet including food (Parkin *et al.*, 1991). Food is the important source of nitrosamine, which is a carcinogen formed by the action of N-nitroso compound with secondary amine. In Thailand fermented foods are compose a lot of preservative food such as potassium nitrate and the high level of nitrate may increase cancer risk. There are many researches revealed that, some types of food such as meat, vegetable, alcoholic beverage, tobacco including medicine are sources of nitrosamines (Taylor and Lijnsky, 1975; Mangino and Scanlan, 1982; Tricker *et al.*, 1984).

Titanium dioxide (TiO₂) is widely used as a photocatalyst, due to its characteristics of chemical and physical stability, high photoactivity, non-toxicity and reusable (Amarnath *et al.*, 2013). Moreover, it is one of the most common photocatalyst used in various applications such as air purification, water purification, anti-bacterial agents, self-cleaning, sterilization and removal nitrate from waste water (Haider *et al.*, 2019). Anatase phase of TiO₂ has shown interesting photosensitivity and catalytic activity. However, poor visible light absorption and large band gap energy (3.2eV) are limitations for anatase (Bianchi *et al.*, 2014). The photocatalytic efficiency of anatase can enhanced by doping process. Recently, many researchers try to introduce various element, including nitrogen into framework of TiO₂ and other photocatalysts (Finazzi *et al.*, 2008; Jin *et al.*, 2009) There are several techniques to add nitrogen into TiO₂. One of the most widely used technique is chemical doping.

Many researchers have been studied the synthesis method for finding anatase phase and nanoparticle sizes (Dhandapani *et al.*, 2014). Sol-gel method is the most common technique used for synthesis of TiO₂ in anatase phase due to this process provides chemical homogeneity and allows the formation of nanostructured materials (Wang and Ying, 1999; Peng *et al.*,

2005). In this work have been synthesized the N-TiO₂ by sol-gel method using titanium (IV) n-butoxide as the precursor and ammonium nitrate as the nitrogen source to obtain anatase phase with nanoparticle size and formed the N-TiO₂ workpieces for using as a catalyst in the photocatalytic efficiency test.

Materials and Methods

Materials

For the N-TiO₂ photocatalysts synthesis, the precursor was used a titanium (IV) n-butoxide 99% (Aldrich), ammonium nitrate (KSK Chemical and Laboratory Appliance) as the nitrogen source. The solvent was ethanol (RCL Labscan Limited), distilled water was used to perform the hydrolysis and acetic acid (RCL Labscan Limited) was used as a catalyst. Polyvinyl alcohol (KSK Chemical and Laboratory Appliance) was used as a binder for forming process. Moreover, potassium nitrate was used to test the photocatalytic activity.

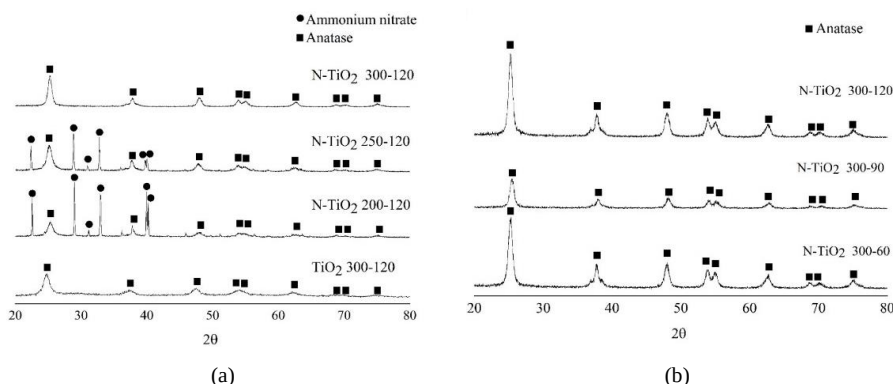
Preparation of N-TiO₂

N-TiO₂ photocatalysts were prepared by sol-gel method. The synthesis process was started by mixing 34 ml of titanium (IV) n-butoxide with 83 ml of ethanol and 6 ml of acetic acid. A solution of ammonium nitrate 12 g dissolved in distilled water 27 ml was taken as the second precursor solution. Then, the second solution was added drop wise into the first solution under vigorous stirring. The obtained gel was aged at room temperature for 24 h. After that, the sample was dried in the oven at 110°C overnight.

A dried sample was put into an alumina crucible and placed into a furnace calcined at low temperature: 200, 250, and 300°C for 60, 90, and 120 min with the heating rate of 3°C per minute. Table 1 showed preparation conditions of samples after calcination at different temperature and time.

Table 1. Preparation conditions and phase composition of TiO₂ and N-TiO₂ photocatalysts

Sample	Calcination conditions		Phase composition
	Temperature (°C)	Time (min)	
N-TiO ₂ (200-60)	200	60	Anatase and Ammonium nitrate
N-TiO ₂ (200-90)	200	90	Anatase and Ammonium nitrate
N-TiO ₂ (200-120)	200	120	Anatase and Ammonium nitrate
N-TiO ₂ (250-60)	250	60	Anatase and Ammonium nitrate
N-TiO ₂ (250-90)	250	90	Anatase and Ammonium nitrate
N-TiO ₂ (250-120)	250	120	Anatase and Ammonium nitrate
N-TiO ₂ (300-60)	300	60	Anatase
N-TiO ₂ (300-90)	300	90	Anatase
N-TiO ₂ (300-120)	300	120	Anatase
TiO ₂ (300-60)	300	60	Anatase
TiO ₂ (300-90)	300	90	Anatase
TiO ₂ (300-120)	300	120	Anatase

**Figure 1. XRD patterns of N-TiO₂ (a) calcined at different temperature (b) calcined at 300°C in different time**

Forming N-TiO₂ Workpiece

A 3 g of polyvinyl alcohol dissolved in distilled water 100 ml. The solution was stirred and boiled on the hot plate at 80°C for 24 h. Then, 5 g of N-TiO₂ powder was mixed together with 5 ml of distilled water and 2.2 mL of polyvinyl alcohol solution. After that, the N-TiO₂ slip was mixed with the ball mill for 24 h. Finally, sponges (2×3×0.5 cm) were dipped in N-TiO₂ slip and dried for 24 h in the oven at 110°C.

Photocatalytic Activity

Photocatalytic performances of photocatalysts were measured by the photodegradation of nitrate in potassium nitrate solution under visible light irradiation

(LED). In each experiment, 1 piece of N-TiO₂ photocatalyst was dipped in 50 ml of potassium nitrate solution (50 ppm) with continuous stirred. After photocatalytic activity, the change of nitrate concentration was measured by Ion Chromatography (IC conductivity Dionex ICS 5000).

Results and Discussion

The phase structures of the samples were shown in Table 1 and the XRD patterns of N-TiO₂ and TiO₂ at different temperatures were shown in Figure 1(a). The pattern of N-TiO₂ (250-120) and N-TiO₂ (200-120) are corresponding to the lattice plane of

ammonium nitrate and anatase. Ammonium nitrate was completely decomposed when calcined at 300°C. The peaks position of N-TiO₂ were shift to higher 2θ when compare to the undoped TiO₂, this indicates that the dopant affects to the peak position of TiO₂ due to the substitution of nitrogen atoms in the lattice of TiO₂. XRD patterns of N-TiO₂ calcined at 300°C in the different reaction time were shown in Figure 1(b). In addition, the highest phase of anatase was obtained at reaction time 120 min. Therefore, the

calcination temperature at 300°C is optimum conditions.

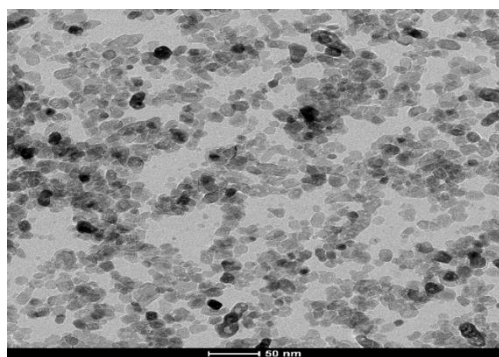
The transmission electron microscope (TEM) images of synthesized N-TiO₂ nanoparticles by sol-gel method are shown in Figures 2(a) and 2(b). The nanoparticles well dispersed and particles size distribution are uniform with average size of 20 nm.

In addition, elemental analysis EDS is used to confirm the composition of N-TiO₂ as shown in Figure 3, the amount of titanium, oxygen and nitrogen content was found in photocatalyst samples.

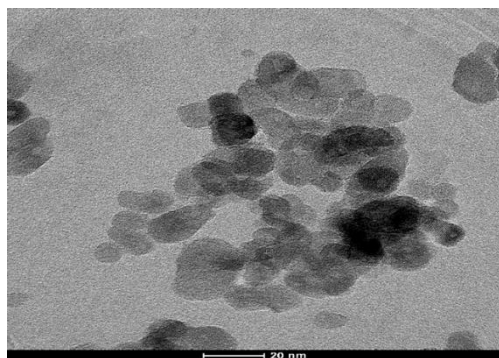
The specific surface area showed in Table 2. The sample N-TiO₂ (300-120) obtained the highest specific surface area 104.18 m²/g calculated by Brunauer-Emmett-Teller (BET). The pore volume is 0.19 cm³/g

Table 2. BET surface area of N-TiO₂ calcined at 300°C

Sample	Specific surface area (m ² /g)
N-TiO ₂ (300-60)	101.75
N-TiO ₂ (300-90)	90.20
N-TiO ₂ (300-120)	104.18



(a)



(b)

Figure 2. TEM images of N-TiO₂ (300-120) (a) at 10,000X (b) at 50,000X

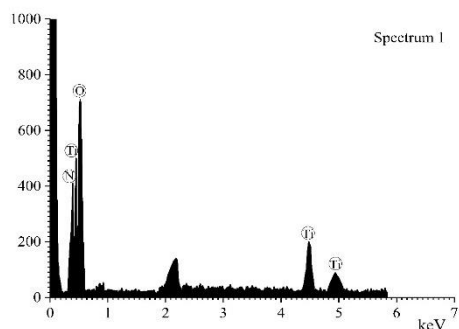


Figure 3. EDS peak of N-TiO₂ (300-120) workpiece

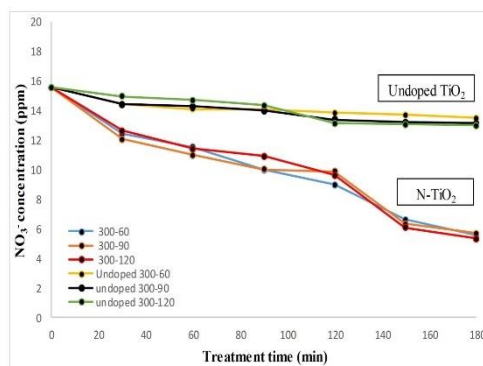


Figure 4. Reaction profiles of nitrate removal for N-TiO₂ and undoped TiO₂

Table 3. Nitrate conversion and products selectivity

Catalyst	Nitrate Concentration		Conversion (%)	Selectivity%		
	Before Treatment	After Treatment		NO ₂ ⁻	NH ₄ ⁺	N ₂
N-TiO ₂ (300-60)	15.57	5.61	63.97	0.81	50.18	49.01
N-TiO ₂ (300-90)	15.57	5.71	63.32	0.83	56.72	42.45
N-TiO ₂ (300-120)	15.57	5.35	65.63	0.73	74.26	25.01
TiO ₂ (300-60)	15.57	13.51	13.23	0.67	71.89	27.44
TiO ₂ (300-90)	15.57	13.15	15.54	0.14	35.13	64.73
TiO ₂ (300-120)	15.57	13.01	16.44	0.86	22.37	76.77

and average pore diameter is 7.44 nm. These results indicate that N-TiO₂ has high specific surface area and small average pore size diameter. Moreover, the presence of larger surface area provide the higher photocatalytic activity due to the development of surface functionalities.

According to Figure 4, the concentration of nitrate significantly decreased. In term of doping, the photocatalytic efficiency of N-TiO₂ photocatalysts are higher than undoped samples. From Table 3, The N-TiO₂ (300-120) shows the greatest photoactivity with the degradation rate of nitrate reaches to 65.63% in 180 min and all catalysts produced nitrite, ammonium and nitrogen as selectivity products.

Conclusions

In this work was studied the effects of temperature and time with various conditions to investigate the optimum calcined temperature and time in order to obtain N-TiO₂ nanoparticles photocatalysts. The results show that, the N-TiO₂ nanoparticles with anatase phase was successfully synthesized by sol-gel method. After calcination at 300°C with reaction time of 60 min, single anatase phase was formed and ammonium nitrate completely decomposed confirmed by XRD. The highest amount of anatase phase was obtained after a reaction time of 120 min. The results of TEM showed the particles size were uniformly distributed with the average of 20 nm. Moreover, the highest specific surface area was obtained with the highest photocatalytic activity after calcination at 300°C for 120 min. The photocatalytic activity under visible light

for nitrate degradation from potassium nitrate solution showed the nitrate degradation rate of N-TiO₂ (300-120) reaches to 65.63% in 180 min higher than undoped samples.

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