การนำไทเทเนียมไดออกไซด์เจือไนโตรเจนไปใช้เป็นตัวเร่งปฏิกิริยาด้วยแสง เพื่อย่อยสลายสารประกอบ benz[a]anthracene

PHOTOCATALYTIC DEGRADATION OF BENZ[a]ANTHRACENE BY USING N-DOPED TiO_2

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บทคัดย่อ: ภายใต้แสงวิซิเบิล ไทเทเนียมไดออกไซด์เจือไนโตรเจน (N-doped TiO_2) ซึ่งถูกเผาที่อุณหภูมิ 400 องศาเซลเซียส สามารถเร่งปฏิกิริยาการย่อยสลายสารประกอบ benz[a]anthracene ได้ร้อยละ 96 ภายในเวลา 120 นาที โดยที่ตัวเร่งปฏิกิริยาทั้งหมดจะเตรียมโดยวิธีโซล-เจล ซึ่งใช้ Titanium(IV) bis (ethyl acetoacetato)diisopropoxide เป็นสารตั้งต้น และสารละลายแอมโมเนียเป็นแหล่งให้ไนโตรเจน การพิสูจน์เอกลักษณ์ของตัวอย่างโดยวิธีการเลี้ยวเบนด้วยรังสีเอ็กซ์ (XRD) และกล้องจุลทรรศน์อิเล็กตรอนแบบส่องผ่าน (TEM) สามารถยืนยันโครงสร้างของ N-doped TiO_2 การเปลี่ยนแปลงเฟสของ N-doped TiO_2 จากแอนาเทสไปสู่รูไทล์ เมื่อใช้อุณหภูมิเผาที่สูงขึ้นจาก 300 องศาเซลเซียส ถึง 700 องศาเซลเซียส และขนาดของ N-doped TiO_2 อยู่ในช่วง 9-51 นาโนเมตร ซึ่งขึ้นกับอุณหภูมิในการเผา โดยคำนวณจากสมการ Sherrer และจากข้อมูลทางสเปกโทรโฟโตเมตรี พบว่า N-doped TiO_2 ซึ่งถูกเผาที่อุณหภูมิ 400 องศาเซลเซียส ปรากฏแถบการดูดกลืนแสงในช่วงแสงวิซิเบิล ในขณะที่ N-doped TiO_2 ซึ่งถูกเผาที่อุณหภูมิอื่น รวมทั้ง P-25 TiO_2 ไม่ปรากฏแถบการดูดกลืนแสงในช่วงวิซิเบิล นอกจากนี้ข้อมูลจากเอ็กซ์เรย์โฟโตอิเล็กตรอนสเปกโทรสโคปี (XPS) พบว่า มีพันธะระหว่าง Ti-N เกิดขึ้นที่ค่าพลังงานยึดเหนี่ยว 397 อิเล็กตรอนโวลต์

Abstract: Under visible light, N-doped TiO_2 calcined at 400 ^oC catalyzed the degradation reaction of benz[a]anthracene with 96% conversion for 120 min. All catalysts, N-doped TiO_2, were prepared via sol-gel process by using Titanium(IV) bis(ethyl acetoacetato)diisopropoxide as a titania precursor and ammonia solution as a nitrogen source. N-doped TiO_2 was calcined with different temperatures from 300 ^oC to 700 ^oC and then characterized by various techniques, namely XRD, TEM, UV-vis reflection and XPS. All of these techniques suggested that there were two major phases, anatase and rutile, of N-doped TiO_2. At low calcination temperature anatase phase was a main phase at a 2θ of 25.7^o while with the increasing temperature the phase transition to rutile occurred and was discernible at a 2θ of 27.6^o. The particle sizes were calculated by Sherrer's equation and showed in the range of 9-51 nm, depending on calcination temperature. N-doped TiO_2 calcined at 400 ^oC exhibited large broad band whilst the other catalysts did not show any broad band in visible region, including commercial P-25 TiO_2. It was found that nitrogen bound directly to titanium in TiO_2 lattice, observed at binding energy of 397 eV.

Introduction: TiO_2 has been widely used as a photocatalyst which generates strong oxidizing species further reacting with water molecules or hydroxyl ions absorbed on the surface of TiO_2 in order to degrade the organic compounds under UV illumination. Although

TiO_2 takes some advantages of its properties such as high stability, low toxicity, low cost and high efficiency for organic degradation reaction, it has still the wide band gap energies especially 3.2 eV for anatase phase, which can be operated only under UV light. Therefore, many recent researches have been focused on band narrowing of TiO_2 by doping with metal cations [1] or anion species [2] so as to improve catalytic activity under visible light because of only ~5% of UV in solar light [3].

Polycyclic Aromatic Hydrocarbons (PAHs) are ubiquitously distributed in atmosphere [4], soil [5] as well as water [6] in environment. Most of them are considered as carcinogenic, mutagenic and teratogenic compounds [4]. Many currently environmental researches indicated that PAHs have posed a severe threat to the human health, especially more fused benzene ring species because of non-polar compounds easy to seep into human body. As for benz[a]anthracene, one of the PAH compounds, it is weakly carcinogenic and mutagenic in experimental animals [7].

In this work, nitrogen doping in TiO_2 lattice has been presented to use as a photocatalyst more sensitive to visible light than unmodified TiO_2. N-doped TiO_2 was synthesized via sol-gel method that is easy to handle at room temperature and suitable for preparing nanomaterials. The as-prepared N-doped TiO_2 and commercial P-25 TiO_2 are further employed to catalyze the photodegradation reaction of benz[a]anthracene under visible light.

Methodology: All N-doped TiO_2 catalysts were prepared by sol-gel method. Initially, 10 ml of Titanium(IV) bis(ethyl acetoacetato)diisopropoxide was stirred with 400 rpm at 30 ^{o}C and then 5 ml of 25% ammonia solution was gradually added into the titanium alkoxide precursor. This system was held constantly for 1 hr. The dried-gel precursor was heated at 120 ^{o}C for 1 hr, followed by calcination at various temperatures from 300 ^{o}C to 700 ^{o}C. All of the catalysts were characterized, including commercial P-25 TiO_2, with XRD, XPS, TEM and UV-vis reflection techniques.

As for the photodegradation reaction, 125 ml of 20 ppm benz[a]anthracene solution, which dissolved in mixed solvent of methanol and water, was used to study the photocatalytic activity of 0.1000 g of N-doped TiO_2, compared with P-25 TiO_2. The activity was measured in terms of the reducing concentration of benz[a]anthracene during operating time, 5 h, by following the fluorescent phenomenon at λ_{em} of 527 nm.

Results, Discussion and Conclusion: The XRD spectra (Figure 1) show that the anatase phase of N-doped TiO_2 appears at 2θ of 25.4^{o} consistent with (101) plane, which is prominent at 400 ^{o}C, and the other phase at 500 ^{o}C, rutile, starts to be discernible at 2θ of 27.6^{o} consistent with (110) plane, continually increasing the intensity at higher calcination temperature. The commercial P-25 TiO_2 has both anatase and rutile phases but the former has a higher intensity. Moreover, the calcination temperature has also the effect not only on the crystalline size of N-doped TiO_2 but the percentage of anatase phase as well. With elevating temperature, the crystalline size, calculated with the Scherrer's equation [8], increases while the content of anatase phase, caculated with the Spurr-Myers equation [9], decreases (Table 1)

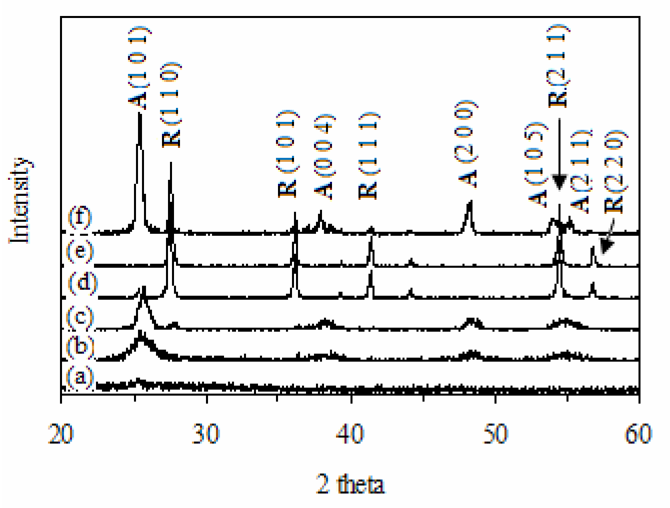

Figure 1 XRD patterns of N-doped TiO_2 calcined at different temperatures (a) 300 °C; (b) 400 °C; (c) 500 °C; (d) 600 °C; (e) 700 °C; (f) P-25 TiO_2.

Table 1 The effect of calcination temperature on crystalline size of N-doped TiO_2 and the content of anatase phase; (A) for anatase, (R) for rutile.

Calcination temperature (°C)	% Anatase	Crystallite size (nm)
400	78.125	8.84 (A)
500	81.576	13.13 (A), 21.53 (R)
600	7.443	50.81 (A), 28.18 (R)
700	1.569	35.53 (R)
P-25	74.834	22.61 (A), 40.86 (R)

The TEM image and histogram (Figure 2) confirm that the crystalline size of N-doped TiO_2 calcined at 400 °C is spherical around 9 nm and particle distribution is in the narrow range.

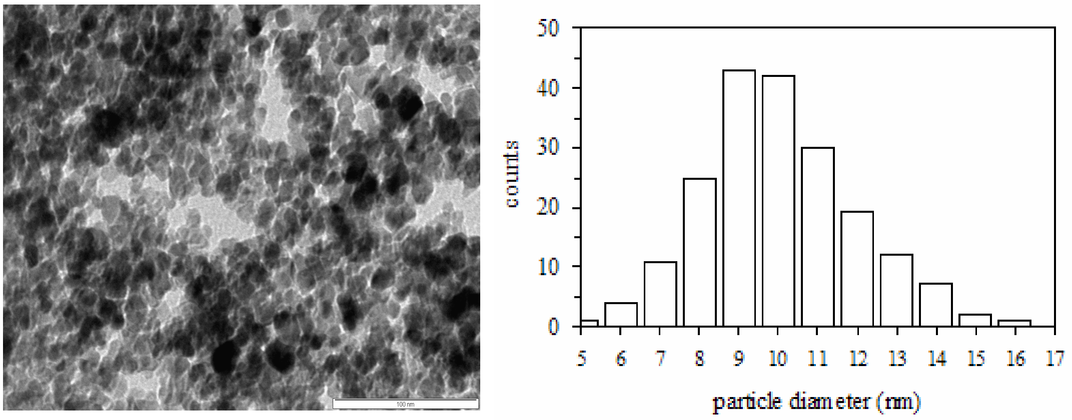

Figure 2 the TEM image and histogram of N-doped TiO_2 calcined at 400 °C

The XPS results (Figure 3) show that, there is Ti-N bond at binding energy of 397 eV in N-doped TiO_2 lattice and chemisorbed N_2 molecule at binding energy 400 eV on N-doped TiO_2 surface [10].

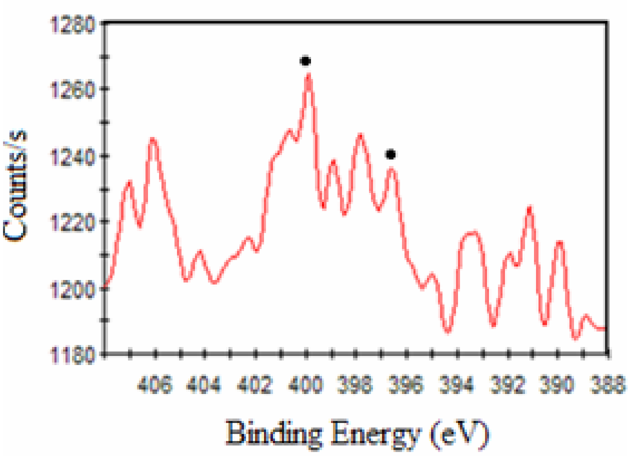

Figure 3 the XPS spectrum of N-doped TiO_2 focusing on binding energy of nitrogen species.

The UV-vis reflection spectra (Figure 4) show that N-doped TiO_2 calcined at 400 °C exhibits a large broad band in visible region, indicating N 2p states make the band gap of TiO_2 narrow by mixing those states with O 2p states. Other catalysts do not show any large broad band. However, N-doped TiO_2 calcined at 700 °C has a small shoulder around 450 nm owing to its rutile phase and the bigger size.

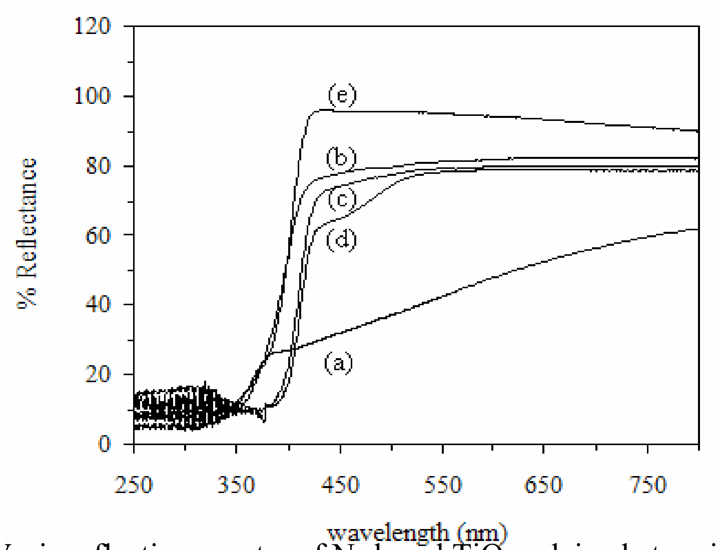

Figure 4 UV-vis reflection spectra of N-doped TiO_2 calcined at various temperatures (a) 400 °C; (b) 500 °C; (c) 600 °C; (d) 700 °C; (e) P-25 TiO_2.

The photocatalytic activity of benz[a]anthracene (Figure 5) illustrates that N-doped TiO_2 calcined at 400 °C has higher efficiency to catalyze the decomposition of benz[a]anthracene with around 96% conversion within 120 min, while the other catalysts provide lower catalytic efficiency. As for the N-doped TiO_2 calcined at 500°C and commercial P-25 TiO_2, the relative concentration of benz[a]anthracene decreases before switching on the lamp because of the adsorption effect on the surface of TiO_2, especially P-25 TiO_2 getting this effect considerably. When the lamp was switched on, the relative concentration of benz[a]anthracene gradually increases in the first few minutes owing to the rate of desorption faster than that of degradation and, then, benz[a]anthracene starts to be degraded. However, it can be largely seen that in the case of no catalyst, besides the effect of photocatalysts, light has also the impact on the degradation of this compound because it is an unstable compound.

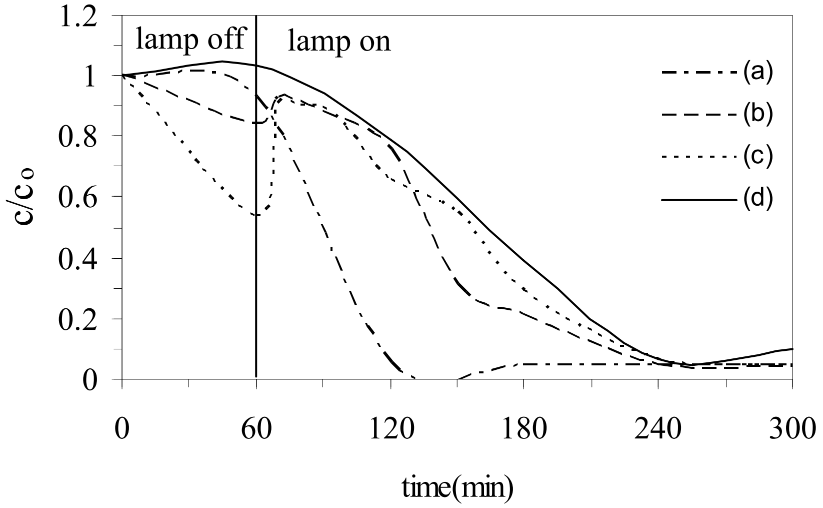

Figure 5 the photocatalytic activity at λ_{em} 527 nm of N-doped TiO_2 calcined at (a) 400 °C; (b) 500 °C; (c) commercial P-25 TiO_2; (d) no catalyst

In summary, nanostructured N-doped TiO_2 has been prepared by sol-gel method. These catalysts are spherical in the range of 9-51 nm and composed of two main phases, anatase and rutile, depending on calcination temperature. The visible absorption efficiency of N-doped TiO_2 has been improved because of the effect of nitrogen doping that causes band narrowing. In part of photodegradation of banz[a]anthracene, N-doped TiO_2 calcined at 400 °C exhibits the highest photocatalytic activity with 96% conversion of benz[a]anthracene.

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Keywords: N-doped TiO_2, sol-gel, photodegradation, benz[a]anthracene

Acknowledgment: We cordially thank the Department of Chemistry and the Department of Physics, Kasetsart University, the Siam Photon Laboratory Thailand, the Center of Excellence for Innovation in Chemistry (PERCH-CIC), Commission on Higher Education, Ministry of Education and the Development and Promotion of Science and Technology Talents (DPST) project for supporting both finance and facilities in this research.