การย่อยสลายเมทิลลีนบลูโดยไทเทเนียมไดออกไซด์เจือไนโตรเจนและซัลเฟอร์ภายใต้แสงวิซิเบิล

DEGRADATION OF METHYLENE BLUE BY USING N-S CO-DOPED TiO_2 UNDER VISIBLE LIGHT

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บทคัดย่อ: การเตรียมตัวเร่งปฏิกิริยาด้วยแสงไทเทเนียมไดออกไซด์เจือไนโตรเจนและซัลเฟอร์โดยวิธีโซล-เจล ในไอโซโพรพานอล ซึ่งใช้ Titanium(IV) isopropoxide เป็นสารตั้งต้น และ ไทโอยูเรียเป็นแหล่งไนโตรเจนและซัลเฟอร์ นำตัวเร่งที่เตรียมได้ไปเผาที่อุณหภูมิ 300-700 องศาเซลเซียส การตรวจสอบคุณลักษณะของ N-S co-doped TiO_2 โดยเทคนิค Raman spectroscopy และ XRD สามารถยืนยันได้ว่าโครงสร้างของตัวเร่งอยู่ในเฟสอนาเทส เมื่ออุณหภูมิสูงขึ้นเริ่มมีการเปลี่ยนเฟสจากอนาเทสเป็นรูไทล์ จากการย่อยสลายเมทิลลีนบลูภายใต้แสงวิซิเบิลพบว่า ตัวเร่งที่ถูกเผ าที่อุณหภูมิ 500 องศาเซลเซียส ซึ่งมีไนโตรเจน 0.028% และซัลเฟอร์ 0.177% สามารถเร่งปฏิกิริยาการย่อยสลายได้ดีกว่าเมื่อเปรียบเทียบกับตัวเร่งที่ถูกเผาที่อุณหภูมิอื่นๆ โดยสามารถย่อยสลายเมทิลลีนบูลได้ 19.49 มิลลิกรัมต่อตัวเร่ง 1 กรัมในเวลา 6 ชั่วโมง

Abtract: N-S co-doped TiO_2 photocatalyst was prepared by sol-gel method using Titanium (IV) isopropoxide as a titania precursor, thiourea as a nitrogen and sulfur source and calcined at various temperature from 300°C to 700°C. Raman spectroscopy and X-ray powder diffraction demonstrated that N-S co-doped TiO_2 catalyst remained in anatase phase. The transition from anatase phase to rutile phase occurred at higher temperature. N-S co-doped TiO_2 calcined at 500°C which contained 0.028%N and 0.177%S, catalytzed the photodegradation reaction of methylene blue in aqueous solution under visible light with the specific degradation activity of 19.49 mg/g of catalyst in 6 hours.

Introduction: It has been documented that dyes are carcinogens and they are affected on aquatic environment and living organisms. The release of these colored waste waters in the ecosystem is a dramatic source of aesthetic pollution, decrease BOD of water and obstruct the route of photosynthesis. Therefore, the improvements of inorganic material to assist dyes degradation are needed to be studied.

At present, TiO_2 is the most widely used in photocatalytic degradation for environmental pollution because of its nontoxicity, long-term stability and inexpensiveness [1]. However, TiO_2 can be activated only under UV-light irradiation that contains 4% of sunlight, owing to its band gap energy of 3.2 eV for anatase phase. Therefore, it is important to improve the photocatalytic reactivity of TiO_2 in order to extend its light absorption into the visible light region. Recently, its has been reported that transition metal cation and nonmetal ions doped into TiO_2 which band gap can be narrowed by these elements doping and make the absorption edge of TiO_2 moving to the visible light region [2]. In order to further improve the photocatalytic activity, co-doped titania with double nonmetal elements has attracted more attention [3].

This research studies the effect of doping nitrogen and sulfur on the photocatalytic activities of TiO_2. N-S co-doped TiO_2 was prepared by sol-gel method. Prepared N-S co-doped TiO_2 catalyst was used to studies the photodegradation of methylene blue in visible light.

Methodology: The N-S co-doped TiO_2 catalyst was prepared by sol-gel method. Initially, 5.5 ml of Titanium (IV) isopropoxide was dissolved in 20 ml of isopropanol, and was added dropwise mixture in titanium precursor. After addition the mixture was stirred for 2 hour. The dried-gel precursor was heated at 120˚C for 2 hours, followed by calcination at various temperatures from 300˚C to 700˚C

All of the catalyst ware characterized by Thermal Gravimetric Analysis (TGA), Raman spectroscopy, X-ray powder diffraction (XRD), Scanning electron microscope (SEM) and Elemental Analysis for the percent corporation of nitrogen, sulfur and carbon.

The photocatalytic activity was determined by the photodegradation of methylene blue in aqueous solution under visible light irradiation. The catalyst (0.1g) was added to 100 ml aqueous solution of methylene blue (20ppm), compared with P-25. The solution collected every 1 hour. The concentration of methylene blue after illumination was determined spectrophotometrically at 664 nm.

Result, Discussion and Conclusion: Figure 1 shows the thermal gravimetric curves of the N-S co-doped TiO_2 powders, which is divided into two regions. The first weight loss between 50◦C-150˚C is due to the physically adsorbed water and alcohol. The second weight loss between 150˚C-300˚C probably owing to strongly adsorbed organic solvent and above 300˚C the weight is constant.

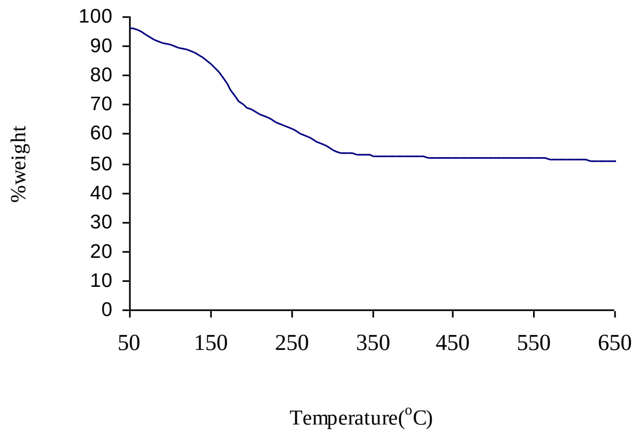

Figure 1. TGA curve of the N-S co-doped TiO_2

The Raman spectrum (Figure 2.) of N-S co-doped TiO_2 calcined at temperature from 300-400˚C show characteristic peak at 397, 515 and 639 cm^{-1} which can be assigned to the anatase phase. After calcined at higher temperature (500°C-600°C), the Raman spectra are similar to the anatase phase. The N-S co-doped TiO_2 calcined at 700°C was transformed into the rutile phase which was confirmed by the present of peak at 455 cm^{-1} and 587 cm^{-1} in the Raman spectrum.

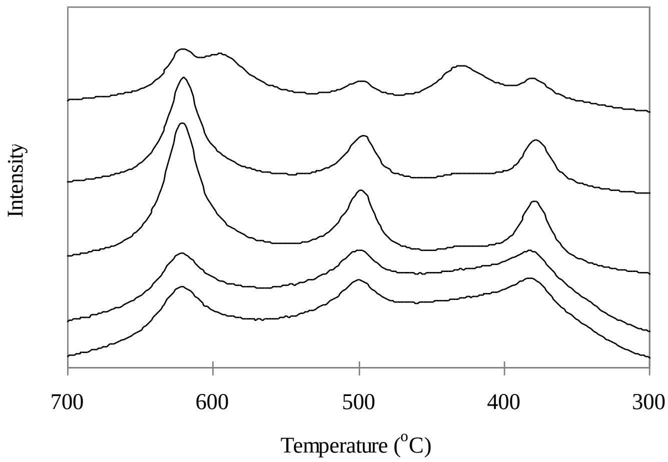

Figure 2. Raman spectra of N-S co-doped TiO_2 calcined at different temperature.

The XRD patterns (Figure 3.) shows the effect of calcination temperature on the phase structures of N-S co-doped TiO_2. It can be seen that the calcination temperature obviously influences phase composition of the catalyst. The appearance of the anatase phase started at the calcination temperature of 300°C. With increasing calcination temperature, the peak intensities of anatase increase and the width of the (101) plane diffraction peak of anatase (2θ =25.4°C) becomes narrower. The result implies that the rutile phase was observed at 500°C (2θ of 27.6°C consistent with (110) plane).

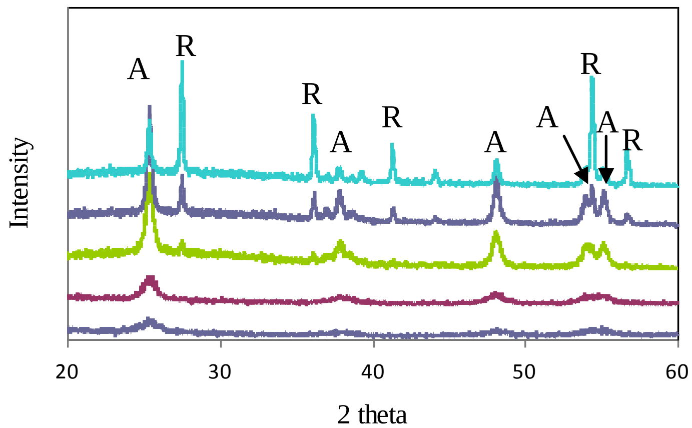

Figure 3. XRD patterns of the N-S co-doped TiO_2 photocatalyst with different calcination temperatures.(a) N-S co-doped TiO_2 300°C: (b) N-S co-doped TiO_2 400°C: (c) N-S co-doped TiO_2 500°C: (d) N-S co-doped TiO_2 600°C: (e) N-S co-doped TiO_2 700°C

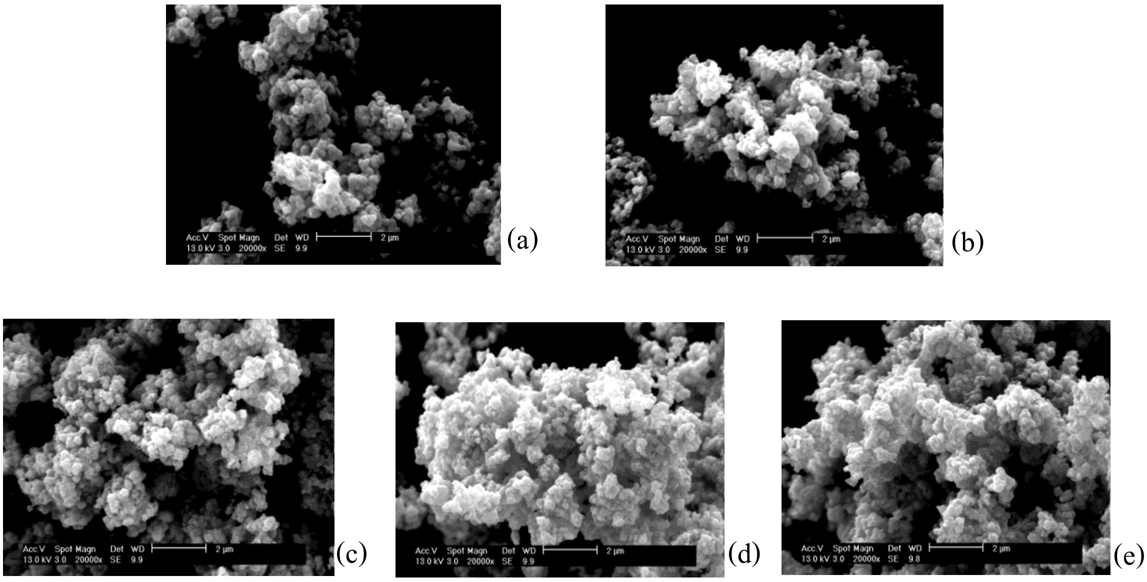

Figure 4. SEM images of TiO_2 prepared at different calcination temperatures. (a) N-S co-doped TiO_2 300˚C: (b) N-S co-doped TiO_2 400˚C: (c) N-S co-doped TiO_2 500˚C: (d) N-S co-doped $TiO_2$600˚C: (e) N-S co-doped TiO_2 700˚C

The SEM images of calcined N-S co-doped at different temperature were presented in Figure 4. Combined with the result of XRD, it is indicated that the crystalline of prepared photocatalyst was agglomerated when the temperature was increased and the morphology of prepared TiO_2 powders is very rough and fluffy grains. Chemical composition analysis using EDX spectroscopy illustrates that the sol-gel prepared sample is mainly composed of Ti and O, with some of nitrogen and sulfur as dopants.

Table 1. Elemental analysis data and Specific degradation activity of methylene blue of N-S co-doped TiO_2

Calcination temperature(°C)	Nitrogen content (%)	Sulfur content (%)	Carbon content (%)	Specific decomposition of methylene blue (mg/g catalyst) in 6 hr.
300	0.391	1.766	0.243	11.690
400	0.067	0.602	0.153	9.835
500	0.028	0.177	0.155	19.486
600	-	0.064	0.067	3.192
700	-	0.026	0.063	-
P-25	-	-	-	12.812

The photocatalytic activity of methylene blue result shows in Table 2 indicates that N-S co-doped TiO_2 catalyst calcined at 500˚C has higher efficiency to catalyze the decomposition of methylene blue with the specific degradation activity of 19.49 mg/g (catalyst) in 6 hours, while the other catalyst provide lower catalytic efficiency. The high photocatalytic activity of the 500˚C sample is due to the composition of anatase phase (0.028%N and 0.177%S) and higher crystallinity than catalyst calcined at lower temperature.

In conclusion, N-S co-doped TiO_2 photocatalysts prepared by sol-gel method can be used for photodegradation reaction of methylene blue in aqueous solution under visible light. The result show that N-S co-doped TiO_2 (500°C) exhibits higher photocatalytic activity than other catalysts.

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