Application of N, S-codoped TiO_2 photocatalyst for degradation of methylene blue

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ABSTRACT

In this study, N, S- codoped titania photocatalyst was synthesized through an efficient and straight forward method using a single source, ammonium sulfate, as modification agent of titanium isopropoxide (TTIP) precursor. The catalyst was characterized by X-ray powder diffractometer (XRD), element Analysis of carbon, hydrogen, nitrogen (CHN), scanning electron microscopy (SEM), diffuse reflectance spectroscopy (DRS), energy dispersive X-ray spectroscopy (EDX) and IR spectroscopy. Visible light photocatalytic studies were carried out using methylene blue as pollutant. The photodegradation efficiency of methylene blue using N, S-codoped TiO_2 were 98%. Also the degradation of methylene blue was tested using P25 photocatalyst for comparison. The result of photocatalytic degradation of methylene blue indicated that photocatalytic activity of N, S-codoped TiO_2 (98%) was better than P25 (82%) photocatalyst, because the band gap of N, S-codoped TiO_2 is lower than of P25 photocatalyst.

Keywords: Photocatalyst, Degradation, N, S-codoped titania, Methylene blue

Introduction

The use of titanium dioxide as a semiconductor photocatalysis is an efficient method for elimination of environmental pollutants especially for degradation of organic pollutants from water [1-7]. While, titanium dioxide has not been applied widely in field of environmentalpollutant control because its high band gap energy (Eg = 3.2ev for crystalline anatase phase) of solar light (visible light). Modification of titanium dioxideto extend its absorption edge toward the visible light region has been the subject of recent research. For solving this problem, titanium dioxide nanoparticle was doped with inorganic elements, such as C [8,9], N [10-13], S [14-18], P [19-21] and halogen atoms [22-24], has been successfully synthesized, and indicated enhanced visible lightphotocatalytic activities than pure TiO_2.

In this paper, we have investigated an application of N, S-codopedTiO_2 for degradation of methylene blue. The structure of this is shown in Fig. 1. Methylene blue is a heterocyclic aromaticchemical compound which used as dermatological agent in the veterinary medicine and a commercial textile dye [25].

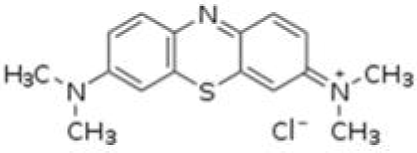

Fig. 1. The structure of methylene blue

Experimental

Materials and methods

All of the Chemicals used in this work were analytical grade reagents and used without further purification. Titanium tetraisopropoxide (TTIP, 98%), ammonium sulfate ($(NH_4)_2SO_4$ 99.5%), glacial acetic acid, ammonia were purchased from Merck company. Titanium tetrachloride ($TiCl_4$, 98%) and commercial photocatalystDegussa P-25 nanoparticles (a mixture of 75% anatase and 25% rutile) were supplied by Fluka and Degussa AG, respectively. Deionized water was used to prepare all solutions.

XRD analysis was performed on a D Jeoljdx-8030 X-ray powder diffractometer with Cu K_α (l= 0.154 nm) radiation (40 kV, 30 mA). To estimate the average crystallite sizes of TiO_2 NPs, the Scherrerequation was applied. The particle morphologies of the as-prepared powders were observed by a Hitachi scanning electron microscopy (SEM) at 30 kV. The FT-IR analyses were carried out on a Shimadzu FTIR-8400S spectrophotometer using a KBr pellet for sample preparation. The EDX result was used to elemental analysis (Philips, XL30) and DRS spectra were prepared via a Shimadzu (MPC-2200) spectrophotometer. For investigation of photocatalytic ability of nanocatalyst, the concentration of 4-NP was determined spectrophotometrically using a double-beam UV-Visible spectrometer (ShimadzuUV-1700) at room temperature in the range of 200-800 nm.

Preparation of the N,S-codoped TiO_2 photocatalyst

The N,S-codoped TiO_2 Photocatalystwas prepared according to under method: 9.8 ml TTIP was added to a 250 ml beaker. After that, 35.2 g of $(NH_4)_2SO_4$ was dissolved in 60 ml of deionized water and was slowly added to above titanium isopropoxide precursor while stirring. The obtained solution was stirred for further 20 min and was exposed under ultrasonic waves for 3 h. Finally, the sample was calcined at 800 ºC for 2h under air with the rate of 5ºC/min to obtain N,S-codopedtitania nanoparticles [26].

Photocatalysisactivity test

The Photocatalysis activity tests were carried out in a photoreactor with methylene blue ormethyl as environmental pollutants by using as-prepared TiO_2. A 400W high-pressure Hg lamp was used as visible light irradiation source. 0.02 g Photocatalyst powder was added to 50ml aqueous solution of dyes (5mg.L^{-1}). The suspension was stirred for 1h in the dark to establish a dyeadsorption – desorption equilibrium. Samples of 3ml were collected from the suspension and were immediately centrifuged at 14000rpm for 20min. The concentration of dyes after illumination was determined spectrophotometrically at range 200-800 nm using a UV-vis spectrometer.

RESULT AND DISCUSSION

XRD

The powder XRD pattern (2θ range from 4° to 90°) of the synthesized codoped (N, S) TiO_2sample is shown in Fig. 2. The diffraction peaks at 2θ = 25.33°, 37.75°, 47.95°, 54.13°, 62.72° corresponding to the anatase phase of titania (JCPDS, file No. 21-1272) are observed in the sample calcined at 850°C that displayed pure anatase phase.

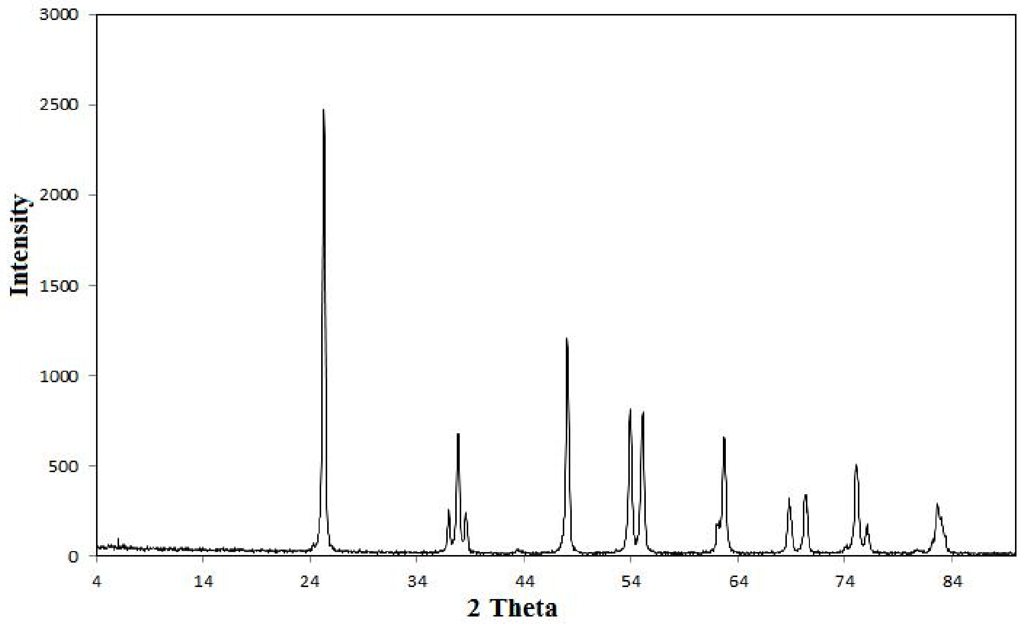

Fig. 2. XRD pattern of N, S-codoped TiO_2Photocatalyst

The average crystallite sizes of particles were estimated by the Scherer's formula as shown below:

$$D = \frac{0.89\lambda}{\beta \mathrm{COS}\theta}$$

Where D is the crystallite size, λ is the X-ray wavelength, β is the broadening of the diffraction peak and θ is the diffraction angle for maximum peak. The calculated mean crystallite size of the N, S-codoped TiO_2 nanoparticles is 36.03 nm.

DRS

Diffuse reflectance spectra of N, S-codoped TiO_2 and P25 are shown in Fig.3.P25 was used as the reference material for comparison purpose. In this image, absorption edge N, S-codoped

TiO_2Photocatalystshifts to the longer wavelength and the visible region.This result indicating that modified Photocatalyst obtained in this study.

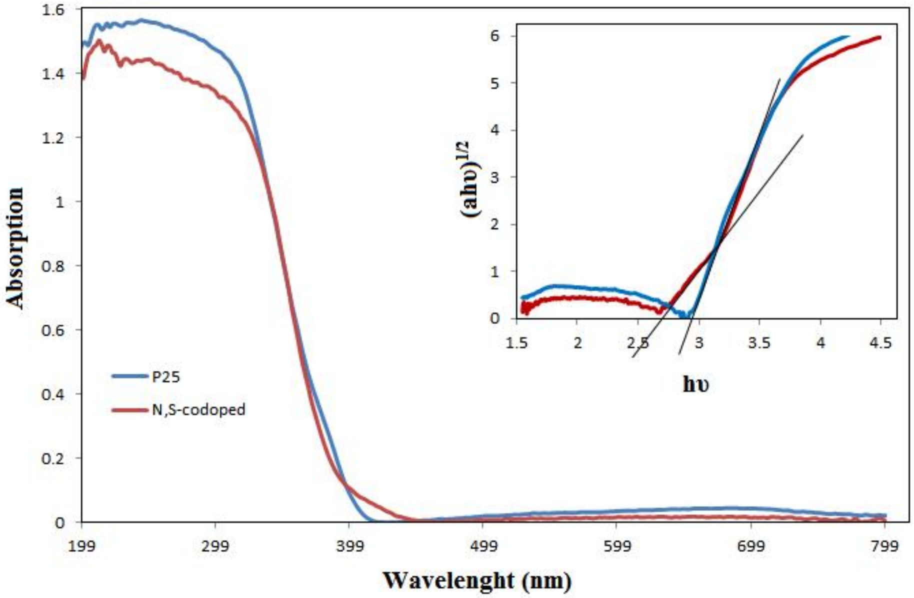

Fig. 3. UV-Vis diffuse reflectance spectra of N, S-codoped TiO_2

FT-IR

The FT-IR spectra of the codoped (N, S) sampleindicated in Fig. 4.The main absorption peaks were located at 3450-3420cm^{-1}, 1640-1630 cm^{-1} and 1060-510 cm^{-1}. The peaks at 3450-3420cm^{-1} and 1640-1630 cm^{-1} were assigned to the stretching vibration and bending vibration of surface –OH group and the band at 580-520 cm^{-1} was assigned to the Ti-O stretching vibration. Ti-O-N and Ti-O-S bonds of the codoped (N, S) sample emerged at 1060 and 1031 cm^{-1},respectively. Moreover, The FT-IR spectra displayed that amount of N and S doped in TiO_2 nanoparticle is small.

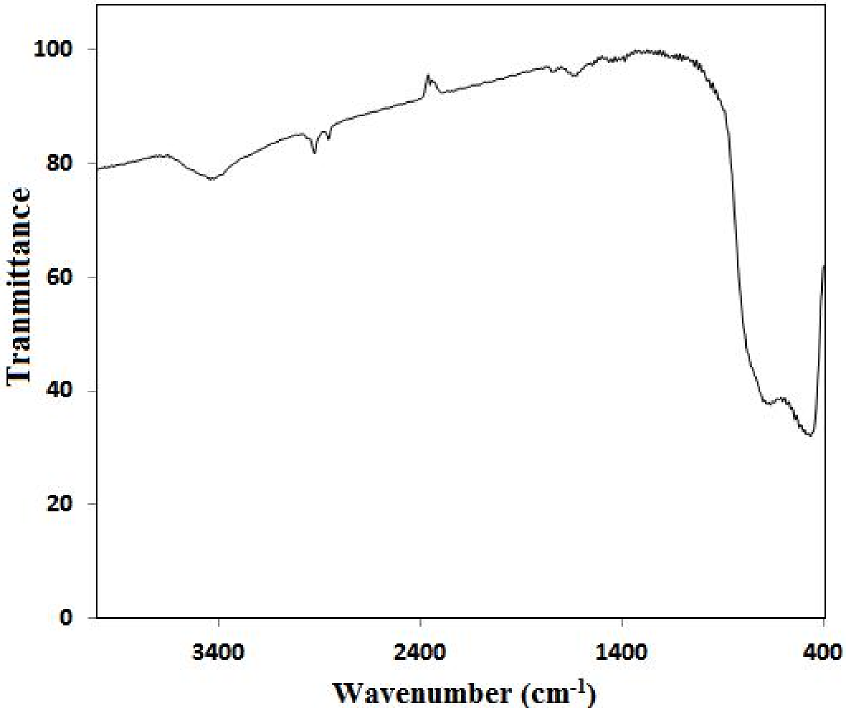

Fig. 4.FT-IR spectra of N, S-codoped TiO_2Photocatalyst

SEM

The surface morphological study of the TiO_2Photocatalyst was carried out using SEM image. Fig.5. shows the SEM image of the N, S-codoped TiO_2nanoparticles. It can be seen that the size of the TiO_2 is in the range of nanometer. The observation of Fig .5indicates thatresult of SEM has consistent well with the result of XRD.

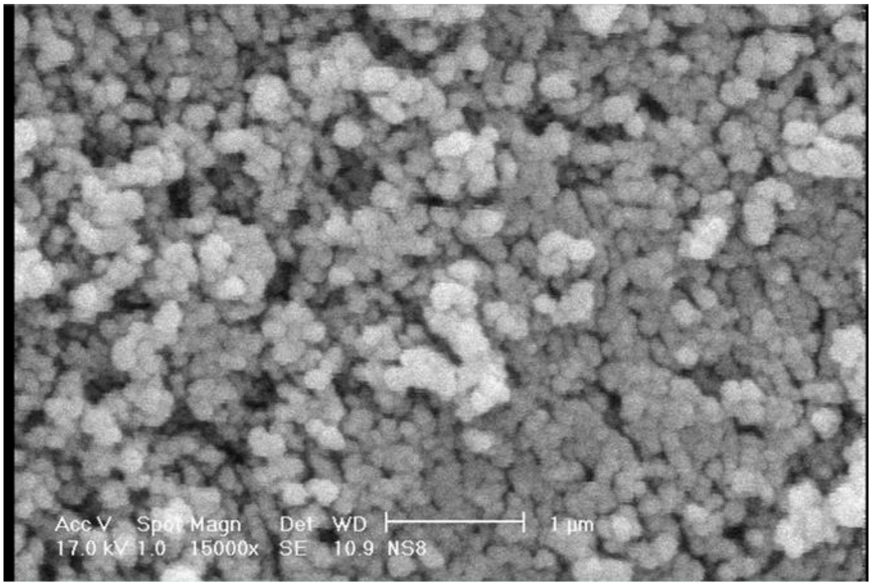

Fig. 5. SEM image of N, S-codoped TiO_2 Photocatalyst

EDX and CHN

The amount of nitrogen and sulfur in TiO_2sample is shown in Table 1.These results taken from EDX and CHN analysis and indicating that amount of N and S doped in TiO_2 nanoparticle is small. These results were agreed with result of FT-IR.

Table 1 The amount of nitrogen and sulfur in TiO_2 sample

Nitrogen content (atomic %)	**Sulfur content (atomic %)**
0.15	0.25

Photocatalytic activity

The photocatalytic activitiy for degradation of methylene blue was investigated in water under visible light using prepared N, S-codoped TiO_2 (Fig. 5-a). The photodegradation efficiency of methylene blue using N, S-codoped TiO_2 were 98%. In addition, the degradation of methylene blue was tested using P25 photocatalyst for comparison (Fig. 6-b). The result of photocatalytic degradation of methylene blue indicated that photocatalytic activity N, S-codoped TiO_2(98%) was better than P25 (82%) photocatalyst, because the band gap of N, S-codoped TiO_2 is lower than of P25 Photocatalyst and synthesized N, S-codopedTiO_2 has pure anatase phase, whereas the P25 sample is mixing of anatase and rutile phase. Anatase phase is stronger structure compared to rutile phase. These two factors, i.e. anatase phase stability and codoping (N, S) made the codoped TiO_2 more photocatalytically active than Degussa P25 photocatalyst.

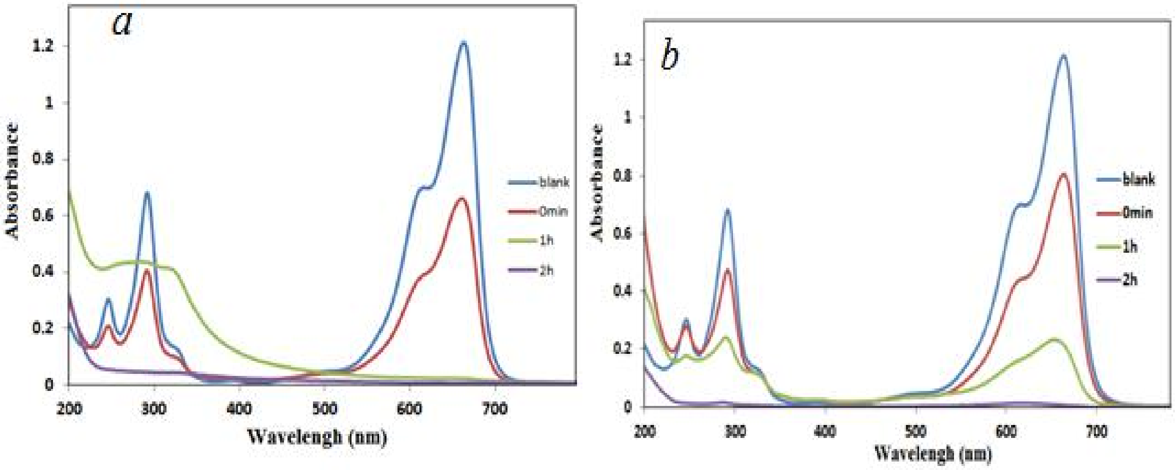

Fig. 6. The UV–vis absorption spectra of methylene blue solutions (a) using N, S-codoped TiO_2 and (b) using Degssap25 after photodegradation with visible light.

Conclusions

Nitrogen, sulfur codoped TiO_2 Photocatalyst with high activity for methylene blue degradation under visible light was synthesized through an efficient and straightforward method using a single source, ammonium sulfate, as modification agent of titanium isopropoxide (TTIP) precursor. In this study we obtained Photocatalyst that acts better than Degussa P25 Photocatalyst due to two factors, i.e. anatase phase stability and codoping (N, S).

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