Photocatalytic degradation of 4-nitrophenol in aqueous N, S-codoped TiO$_2$ suspensions

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Abstract

In this paper we have investigated photocatalytic activity of the N, S-codoped TiO$_2$ nanoparticles for degradation of 4-NP in aqueous. In this method nitrogen and sulfur doping by using a single source, ammonium sulfate as the modification agent of titanium tetrachloride as precursor and the N, S-codoped TiO$_2$ nanoparticles prepared by the sol-gel method. This catalyst was characterized by XRD, SEM, UV- visible and FT-IR.

 Keywords: degradation, 4-nitrophenole, N-S-codoped TiO$_2$, photocatalytic

1. Introduction

Semiconductor photocatalysis is an efficient method for the chemical utilization of solar energy. TiO$_2$, among various photocatalysts, is most frequently employed owing to its cheapness, nontoxicity, and structural stability [1–5].

However, the widespread technological use of TiO$_2$ is impaired by its wide band gap (ca. 3.2 eV for crystalline anatase phase) which requires the use of UV light during the reaction while the solar spectrum usually contains about 4% UV light, thus limiting the possibility of employing solar light in TiO$_2$ photocatalysis Besides, the low quantum efficiency of the TiO2 also limited its application. Therefore for solve this problem, titanium dioxide nanoparticle doped with inorganic elements, such as C, N ,S, P and halogen atoms, has been successfully synthesized, and indicated enhanced visible light photocatalytic activities than pure TiO$_2$.In this paper we have investigated an application of N, S-codoped TiO$_2$ for degradation of 4-nitrophenol as environmental pollution. 4-Nitrophenol (4-NP) is a toxic and bio-refractory pollutant which can cause considerable damage to the ecosystem and human health. It can damage the central nervous system, liver, kidney and blood of humans and animals. 4-NP and its derivatives are used in the production of pesticides, and as insecticides and herbicides [6]. Nitroaromatics are used in the production of explosives, and 4-NP is used in the production of many synthetic dyes [7]. Therefore, 4-NP and its derivatives are common pollutants in many natural water and industrial wastewater.

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2. EXPERIMENTAL
2.1. Preparation of N, S-codoped TiO$_2$ nanoparticles

Titanium tetrachloride (TiCl$_4$, analytical reagent grade) was used as titanium precursor. Commercially available reagents were obtained from Aldrich and used without further purification. The N,S-codoped titania samples were prepared by hydrolysis TiCl$_4$ with

ammonia in water solution in the presence of glacial acetic acid and ammonium sulfate ($(NH_4)_2SO_4$). In a typical procedure, 25 mL of dilute aqueous solution of $TiCl_4$ (3.0 mol L^{-1}) was carefully added into 150 mL deionized water with gentle stirring in ice-water bath to avoid a drastic hydrolysis of $TiCl_4$ in water at room temperature. Subsequently, 4.5 mL of glacial acetic acid and 10 g ammonium sulfate was added into the solution, and then the solution was heated to 323 K. After that, a 35% (w/w) solution of ammonia was added dropwise with vigorous stirring until pH8, and then the mixed solution was quickly cooled down to ambient temperature (about 298 K) by rinsed with running water. After aging in the mother liquor for a few days, the resultant slurry was suction-filtered and washed with distilled water until pH 7 and then washed carefully with absolute ethanol for three times The N, S-codoped titania samples were finally obtained after the as-prepared filter residue being vacuum-dried at 353 K for 12 h, followed by calcination at 450⬚ for 3 h with the rate of 10 K min^{-1}[8].

2.2. Photocatalysis studies

The visible light photocatalytic activity was performed by the following approach. In a typical experiment 0.1g of calcined sample was dispersed in 50ml of 4-nitrophenol solution having a concentration 2ppm and PH6. The above suspension was stirred for 30min in the dark to obtain adsorption-desorption equilibrium to eliminate the error due to any initial adsorption effect. Then this was irradiated in a 400W high-pressure Hg lamp.Degradation was monitored by taking 3ml aliquots at different intervals of time. These aliquots were centrifuged for 15 min prior to absorbance measurements in order to eliminate the error due to scattering. The concentration of 4-NP was determined spectrophotometrically using a double-beam UV-Visible spectrometer.

3. RESULT AND DISCUSSION
3.1. XRD pattern

Fig.1. Shows the XRD pattern (2θ ranges from 0° to 85°) of the calcined product at 450°C, which can be indicated the anatase phase of the codoped (N, S) sample.
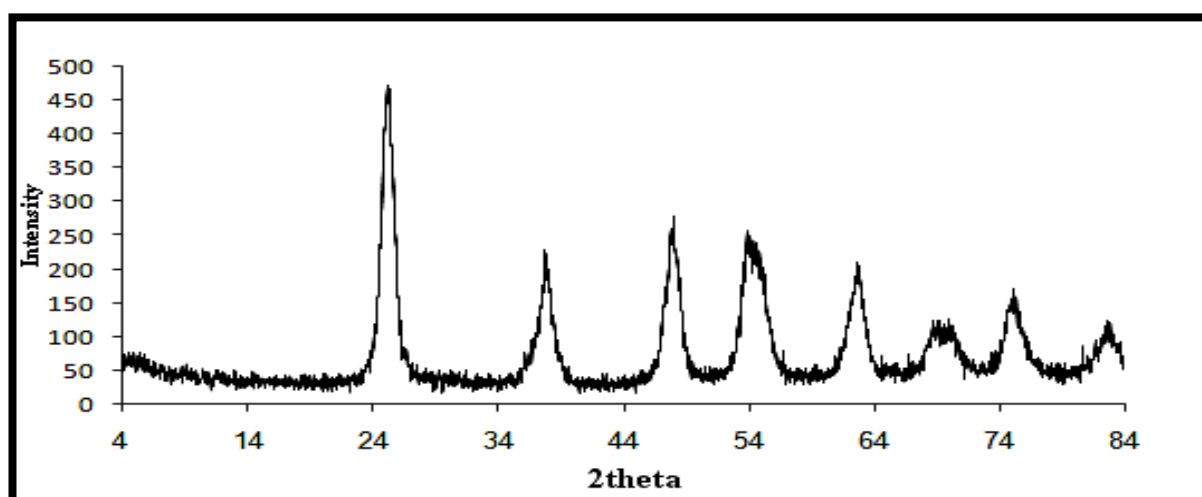
Fig. 1. XRD pattern of the synthesized TiO$_2$ codoped (N, S) nanoparticles

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

$$D \quad \frac{0.89\lambda}{\cos}$$

Where D is the crystallite size, λ is the X-ray wave length, 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 10.81 nm.

3.2. Result of DRS

Diffuse reflectance spectra of N, S-codoped TiO$_2$ and P25 are shown in Fig.2. P25 was used as the reference material for comparison purpose. In this image, absorption edge N, S-codoped TiO$_2$ Photocatalyst shifts to the longer wavelength and the visible region .This result indicating that modified Photocatalyst obtained in this study.
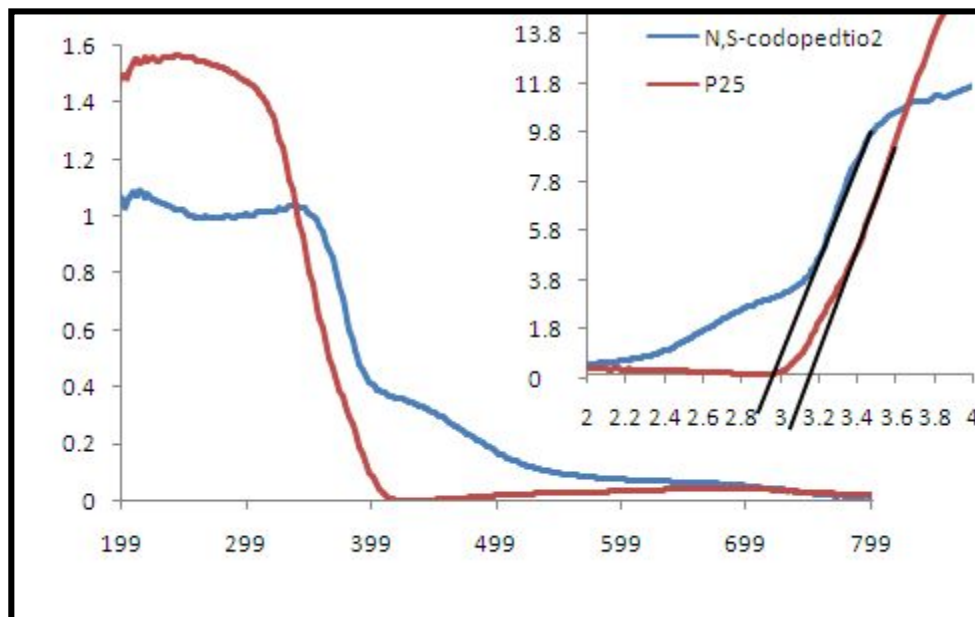

Fig.2. UV-Vis diffuse reflectance spectra of N, S-codoped TiO$_2$

3.3. Result of FT-IR

The FT-IR spectra of the codoped (N, S) sample indicated in Fig. 3.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.
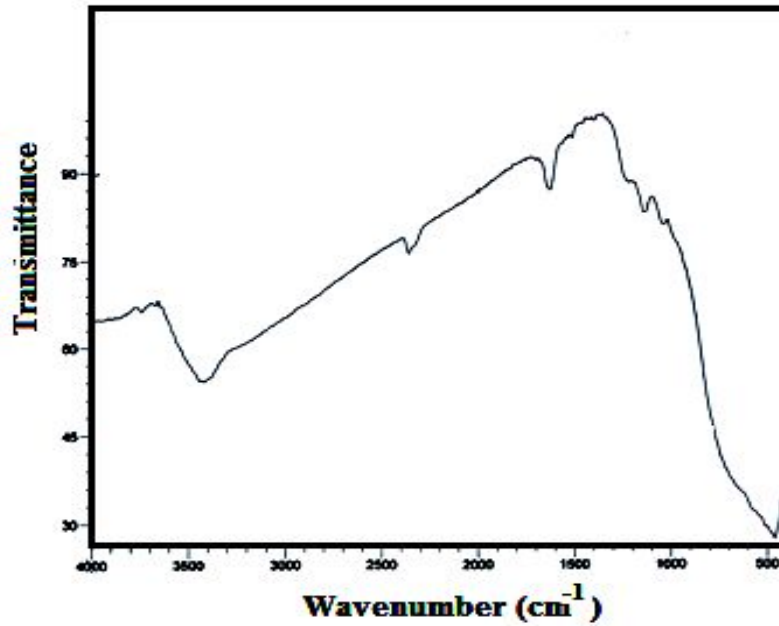
Fig.3. FT-IR spectra of N, S-codoped TiO_2 Photocatalyst

3.4. Result of SEM

SEM image of N, S-codoped TiO_2 at sol-gel method was presented in Fig.4. It is obvious that the TiO_2 crystal was agglomerated significantly. It can be seen that the size of the microsphere TiO_2 is in the range of nanometer. The observation of Fig .4 indicates that result of SEM has consistent well with the result of XRD.
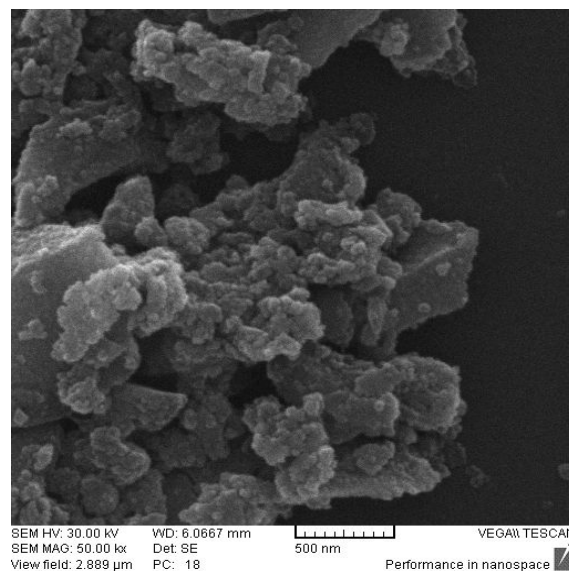

Fig.4. SEM image of N, S-codoped TiO_2 Photocatalyst

3.5. Photocatalytic activity

However, the photocatalytic activity of titania depends upon several factors, such as phase composition (anatase and/or rutile), surface area crystallinity and crystallite size, absorption

properties of the dyes on the surface of TiO_2 used, rate of electron –hole recombination, and the number of electrons created. Which factor dominates the photocatalytic effect of titania is datable. In this study, sample calcined at temperature 450°C shows significantly lower photcatalytic activity than Degussa P25. In this paper band gap TiO_2 (N.S-codoped)sample was shorter than P25, but P25 acting better than N,S-codoped TiO_2 sample, because it was agglomerated significantly(Fig.5-8).
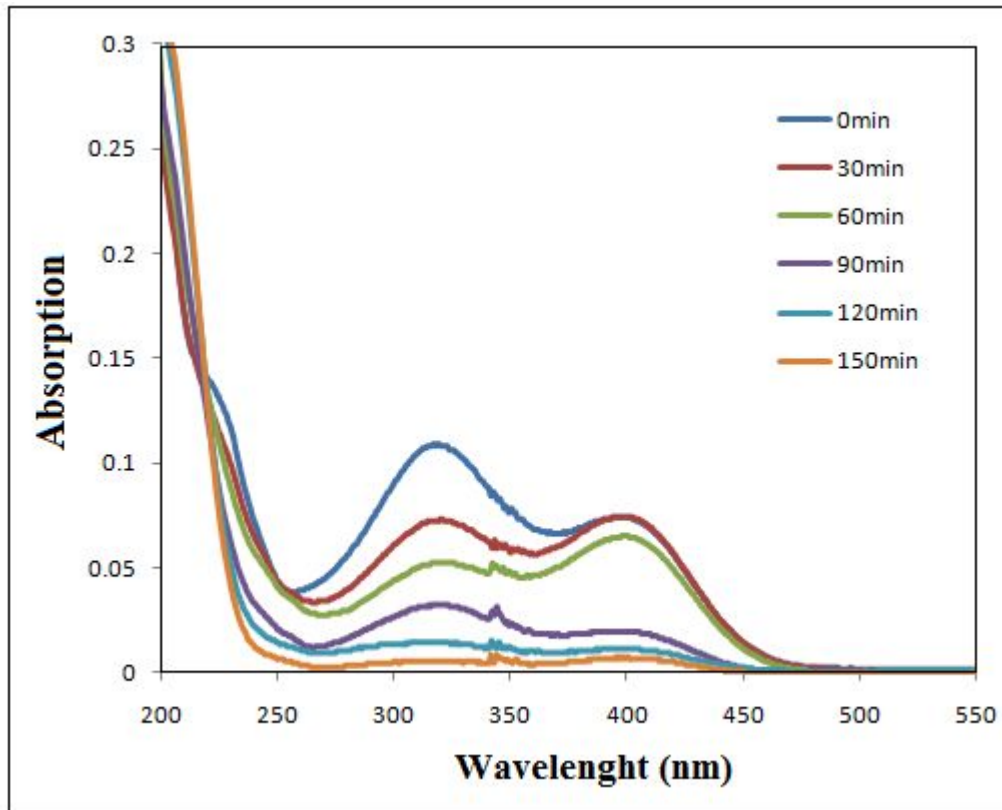

Fig. 5. The UV-vis absorption spectra of 4-NP solution during the degradation by N, S co-doped TiO_2/ Visible process at 25 °C ($C_0 = 2$ ppm, pH=6, 0.1 g/50 mL TiO_2)
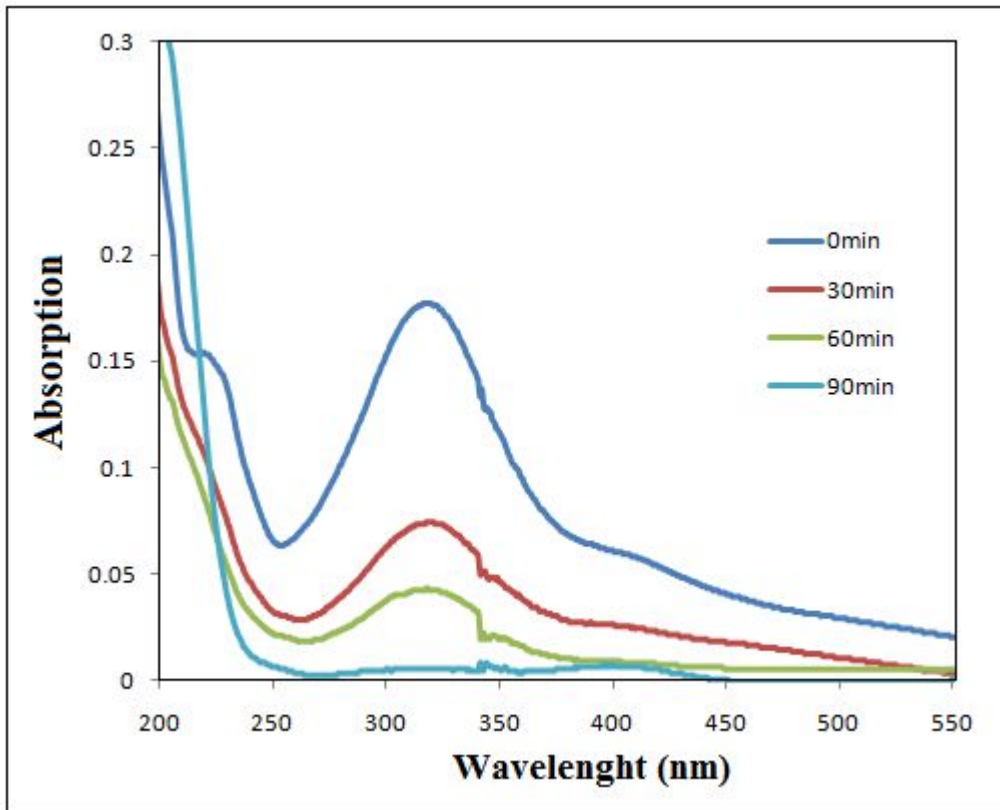
Fig. 6. The UV-vis absorption spectra of 4-NP solution during the degradation by P25/ Visible process at 25 °C ($C_0 = 2$ ppm, pH=6, 0.1 g/50 mL P25)
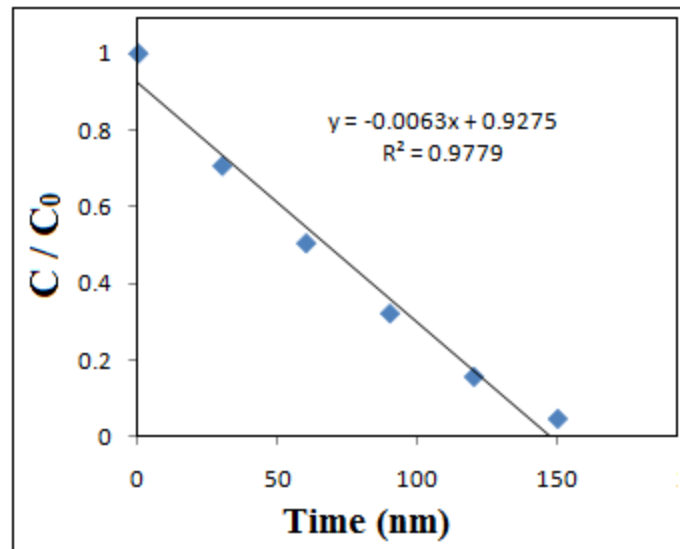

$y = -0.0063x + 0.9275$
$R^2 = 0.9779$

Fig. 7. . Photocatalytic degradation of 4-NP by N, S co-doped TiO_2/ Visible process at 25 °C ($C_0 = 2$ ppm, pH=6, 0.1 g/50 mL TiO_2)
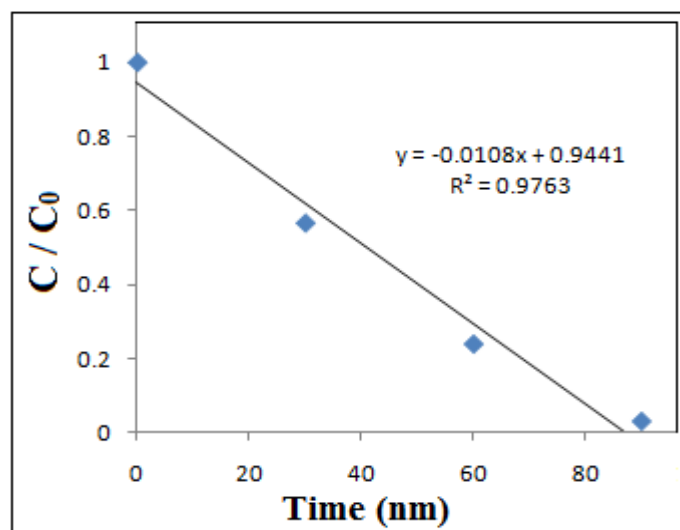
$$y = -0.0108x + 0.9441$$
$$R^2 = 0.9763$$

Fig.8. Photocatalytic degradation of 4-NP by P25/ Visible process at 25 °C ($C_0 = 2$ ppm, pH=6, 0.1 g/50 mL P25)

4. Conclusions

TiO$_2$ (N.S-codoped) nanoparticles have been successfully synthesized through a sol-gel method. In this method nitrogen and sulfur doping by using a single source, ammonium sulfate as the modification agent of titanium tetrachloride as precursor. In this work,we have investigated photocatalytic activity of the N, S-codoped TiO$_2$ nanoparticles for degradation of 4-NP in aqueous .These results indicated that photcatalytic activity Degussa P25 was better than TiO$_2$ (N.S-codoped) nanoparticles.

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