

## Research Article

# Nanocrystalline N-Doped TiO<sub>2</sub> Powders: Mild Hydrothermal Synthesis and Photocatalytic Degradation of Phenol under Visible Light Irradiation

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Nitrogen-doped TiO<sub>2</sub> powders have been prepared using technical guanidine hydrochloride, titanyl sulfate, and urea as precursors via a mild hydrothermal method under initial pressure of 3MPa, 150°C holding for 2h without any postheat treatment for crystallization. The nanocrystalline N-doped TiO<sub>2</sub> powders were composed of anatase TiO<sub>2</sub> by XRD. The grain size was estimated as about 10 nm, and the BET specific surface area of the powder was measured as 154.7 m<sup>2</sup>/g. The UV-visible absorption spectra indicated that the absorption edge of the N-doped TiO<sub>2</sub> powders had been red shifted into the visible light region. The photocatalytic performance of the synthesized powders was evaluated by degradation of phenol under visible light irradiation. And the effects of the catalyst load and the initial pH value on the photodegradation were also investigated.

## 1. Introduction

Water pollution has become a major problem in recent years. The biological, chemical, and physical-chemical water treatment methods are often ineffectively or environmentally incompatible [1, 2]. Heterogeneous photocatalytic oxidation has been considered as one of the effective methods to treat the pollutants in water through the photo-generated hydroxyl radicals and super oxygen species [3, 4]. TiO<sub>2</sub> photocatalyst has attracted much attention due to its low cost, high stability, nontoxicity, and environmental friendly properties [5, 6]. However, TiO<sub>2</sub> can only be excited by UV light ( $\lambda < 387$  nm, accounts only about 5% of sunlight) because of its large band gap of 3.2 eV for anatase which limits its application in practical use. Many methods have been adopted to extend its optical response to visible light (accounts about 45% of sunlight), such as doping with impurities [7–10], sensitizing by dyes [11], and coupling with semiconductors [12].

Doping TiO<sub>2</sub> with various elements is the most effective way to narrow its band gap. Among these dopants, nitrogen has attracted much attention in recent years due to its small ionization energy, comparable atomic size with

oxygen, metastable center formation, and enhanced UV-Vis photocatalytic performance [7]. Many works on the preparation of N-TiO<sub>2</sub> by physical or chemical methods have been published [13–22]. Among these methods, N-TiO<sub>2</sub> powders were mainly prepared either by calcination of TiO<sub>2</sub> powders under nitrogen containing atmosphere or by postheat treatment of the Sol-Gel/hydrothermally prepared amorphous TiO<sub>2</sub> with nitrogen agents at high temperature for both doping nitrogen atoms into the TiO<sub>2</sub> lattice and crystallization. However, calcination under high temperature may cause agglomeration and abnormal growth of crystals which results in small surface area and decreases the number of photoactive sites. So, it is necessary to seek an appropriate route to synthesize N-TiO<sub>2</sub> effectively under mild conditions. However, it is not so easy to dope nitrogen into TiO<sub>2</sub> under mild hydrothermal conditions because the bond energy between Ti–O is greater than that of Ti–N bond [23]. Some researchers have tried to synthesize N-TiO<sub>2</sub> powders by one-step hydrothermal method without postheat treatment in a relatively lower temperature [24]. It was found that N-TiO<sub>2</sub> could be synthesized through one-step hydrothermal method at 150°C for 8 h [25]. N-TiO<sub>2</sub> nanoparticles were prepared

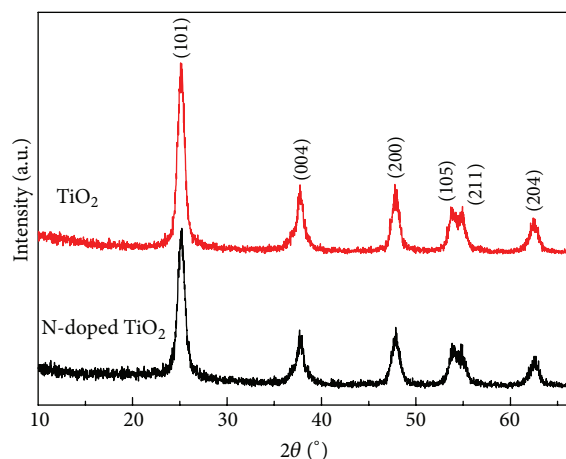


FIGURE 1: XRD patterns of the undoped and N-doped  $\text{TiO}_2$  powders.

by using Degussa P25 and triethanol amine as precursors via hydrothermal method at  $140^\circ\text{C}$  holding for 24 h [26]. So, it always needs longer reaction time in the one-step hydrothermal method to prepare N-doped  $\text{TiO}_2$ .

In this paper, well crystallized N-doped  $\text{TiO}_2$  powders with enhanced visible light absorption have been prepared by a mild hydrothermal method at  $150^\circ\text{C}$  holding for 2 h without any postheat treatment for crystallization. The photocatalytic performance of the synthesized powders was evaluated by degradation of phenol in aqueous solution under visible light irradiation.

## 2. Experimental

N-doped  $\text{TiO}_2$  powders were prepared via a hydrothermal method at  $150^\circ\text{C}$  holding for 2 h. Technical grade  $\text{TiOSO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{CO}(\text{NH}_2)_2$  and  $\text{CH}_5\text{N}_3 \cdot \text{HCl}$  were used as received and without any further purification. In a typical synthesis process, titanyl sulfate (1M), urea (1.5M), and guanidine hydrochloride (3M) were dissolved in 1L distilled water and stirred for 30 min, and then the mixed solution was transferred into an autoclave with an internal volume of 2 L. The initial pressure was set at 3 MPa, and the stirring speed was fixed at 300 r/min. The autoclave was heated to  $150^\circ\text{C}$  holding for 2 h. The obtained suspension was centrifuged and washed with deionized water until no  $\text{SO}_4^{2-}$  was detected in the washes. After drying at  $90^\circ\text{C}$  in air, the yellow colored N-doped powders were obtained. The white undoped  $\text{TiO}_2$  was also synthesized under the same processing parameters.

The synthesized N-doped powders were characterized by X-ray diffraction, Brunauer-Emmett-Teller (BET), Transmission electron microscopy, UV-Visible diffuse reflectance spectra, and X-ray photoelectron spectroscopy. The photocatalytic activity of N-doped powders was evaluated by photodegradation of phenol in aqueous solution under 400~650 nm visible light irradiation with illuminant intensity of  $15.54 \text{ mW/cm}^2$ . Firstly, 0.25 g of N-doped powders were mixed into 100 mL phenol aqueous solution with a concentration of 25 mg/L, and then the suspension was stirred in the

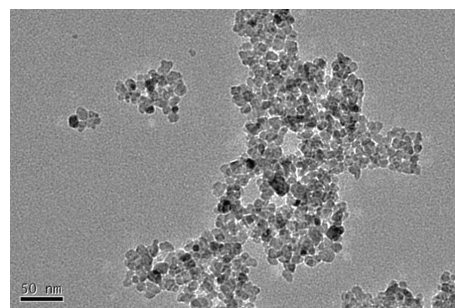


FIGURE 2: TEM micrograph of N-doped  $\text{TiO}_2$  powders.

dark for 2 h to reach the balance of adsorption/desorption. The balanced concentration of phenol was treated as the initial phenol concentration. Then, the light was turned on to start photodegradation. The suspension was sampled at an interval of 2 h and centrifuged to remove the N-doped  $\text{TiO}_2$  particles. The concentration of phenol was measured on a UV-Visible spectrophotometer (TU-1901) at the wavelength of 270 nm to obtain the absorbance of the solution.

## 3. Results and Discussion

Figure 1 shows the XRD patterns of the synthesized pure and N-doped  $\text{TiO}_2$  powders. All the peaks are corresponding to those of anatase. The intensity of the peaks of N- $\text{TiO}_2$  is slightly weakened compared with that of undoped  $\text{TiO}_2$ . From the line broadening of the (101) diffraction peak by Scherrer's method, the grain sizes of undoped and N-doped  $\text{TiO}_2$  are about 9.7 and 10.0 nm, respectively. The specific surface areas for undoped and N-doped  $\text{TiO}_2$  are 150.6 and  $154.7 \text{ m}^2/\text{g}$ , respectively.

Figure 2 shows the TEM micrograph of N-doped  $\text{TiO}_2$  powders. The particles are approximately spherical in shape and 10 nm in size, which is consistent with the results calculated by Scherrer's method.

The UV-Visible absorption spectra of undoped and N-doped  $\text{TiO}_2$  powders are shown in Figure 3(a). It is clear that N-doped  $\text{TiO}_2$  powders exhibit stronger visible light absorption while the undoped  $\text{TiO}_2$  can absorb only UV light. The straight-line extrapolation method was used to determine the light absorption edge of the powders, as indicated in Figure 3(a). The absorption edge of the undoped  $\text{TiO}_2$  is approximately 390 nm while that of N-doped  $\text{TiO}_2$  is around 420 nm. According to the equation  $E_g = 1240/\lambda$  (eV), the band gap energies of the undoped and N-doped  $\text{TiO}_2$  are 3.18 and 2.95 eV, respectively. As  $\text{TiO}_2$  has been considered as an indirect semiconductor [27, 28], the band gap energy of the samples can be estimated by Kubelka-Munk function [29, 30], as shown in Figure 3(b). Band gap energy calculated from the intercept of the tangent lines in the plots are 3.10 and 2.90 eV for undoped and N-doped  $\text{TiO}_2$ , respectively, which is in accordance with the UV-Vis results.

The concentration and the electronic state of nitrogen at the surface of the N-doped  $\text{TiO}_2$  powders were measured by XPS, as shown in Figure 4. The XPS survey spectra as

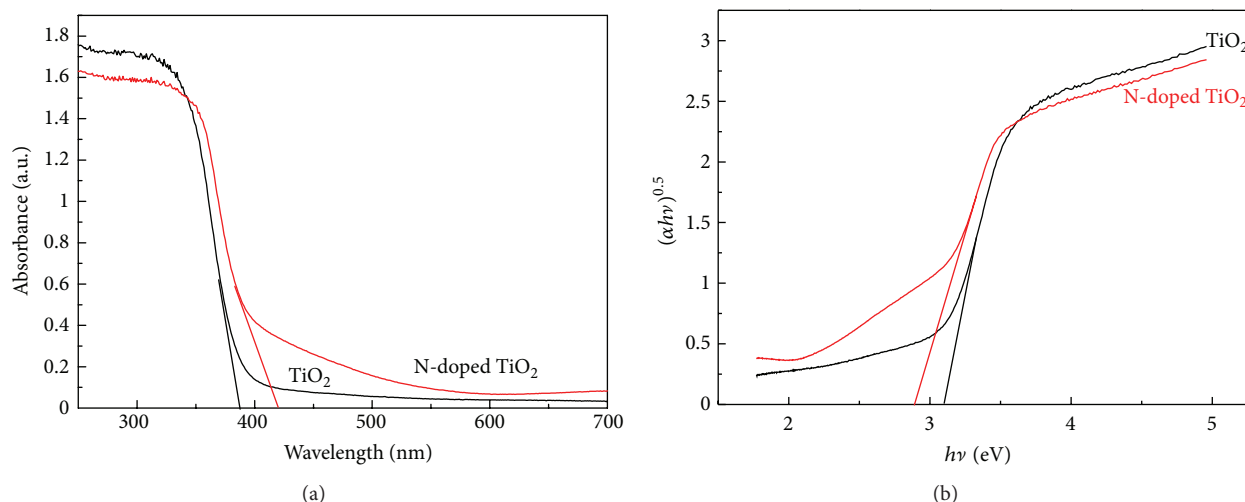


FIGURE 3: (a) UV-Visible absorption spectra of undoped and N-doped  $\text{TiO}_2$  powders and (b) plots of  $(\alpha h\nu)^{0.5}$  versus photoenergy of the synthesized samples.

indicated in Figure 4(a) show that the surface of N-doped  $\text{TiO}_2$  is composed of Ti, O, N, and carbon. The concentration of nitrogen is about 1.6% (atomic percent). Yang et al. [31] suggested that when the doping concentration of nitrogen was less than 2.1% (atomic percent), an isolated N2p states would be created above the O2p valance band, which might contribute to the visible light sensitivity. Figure 4(b) shows the binding energy of N1s located at both 396.0 and 399.9 eV. The weaker peak located at 396.0 eV can be attributed to the Ti–N bond which indicates that nitrogen atoms have been incorporated into the lattice of  $\text{TiO}_2$  [32, 33]. The stronger peak located at 399.9 eV can be assigned to Ti–O–N linkage which is considered as the interstitial nitrogen atoms in the lattice of  $\text{TiO}_2$  and has been reported in many literatures [34–36].

The photodegradation of phenol aqueous solution under different conditions is shown in Figure 5. In order to confirm any possible self-degradation of phenol under visible light irradiation, the light irradiation of phenol solution with the same illumination intensity was processed. It can be seen in Figure 5 that the phenol concentration remains almost unchanged with the elapse of irradiation time. That is, the phenol will not be degraded by the visible light irradiation.

The effect of the phenol adsorption by the catalysts on the photocatalytic degradation process has been investigated by stirring the phenol-catalysts suspensions in the dark for 10 h. The concentration of phenol was decreased only 2% during the 10 h black stirring as indicated in Figure 5. So, the decrease of the concentration of the phenol caused by the adsorption of the catalysts can be ignored. Forty-seven percent of phenol has been degraded by N- $\text{TiO}_2$  powders while that by undoped  $\text{TiO}_2$  is 15%. N-doped  $\text{TiO}_2$  exhibits better photoactivity than that of undoped  $\text{TiO}_2$ , which indicates that nitrogen doping has improved the photocatalytic activity of  $\text{TiO}_2$  in the visible light region.

Catalyst load is an important factor that affects the photocatalytic degradation of phenol. The influence of the load

of photocatalyst was performed by varying the amount of N-doped  $\text{TiO}_2$  from 0.1 to 2.0 g, as indicated in Figure 6. The maximum photocatalytic degradation is obtained when using 0.25 g N-doped  $\text{TiO}_2$  powders. Further increase or decrease, the amount of catalysts will reduce the photodegradation. The results are in agreement with the data published by other researchers [37, 38]. When the amount of the charged catalyst is too high, turbidity will hinder the light penetration and enhance the light scattering [39]; thus, the photocatalytic activity of the catalyst will be reduced due to the decreased light intensity. Besides, the aggregation of particles increases with the increase of the amount of the photocatalyst which may also decrease the total active sites for the adsorption of photos and phenol [34], resulting in the decrease of photodegradation.

The pH value of the aqueous solution affects the surface charge of the catalyst as well as phenol. The effect of pH value on photodegradation of phenol was investigated in the range of 4 to 10 by adjusting the solution with 1 mol/L HCl and NaOH, as shown in Figure 7. The maximum photodegradation is observed at pH = 4, and it can reach 81% after 10 h of visible light irradiation. The similar results were also reported in [40]. Figure 8 shows the zeta potential of N-doped  $\text{TiO}_2$  in phenol aqueous solution at different pH values. The isoelectric point of N-doped  $\text{TiO}_2$  particle is 6.4. According to the isoelectric point of N-doped  $\text{TiO}_2$ , the following reactions may occur on the surface of N-doped  $\text{TiO}_2$  at different pH values:



That is, the surface of N-doped  $\text{TiO}_2$  will be positively charged at pH < 6.4 and negatively charged at pH > 6.4. As the dissociation constants ( $pK_a$ ) of phenol are 9.96 ( $t = 25^\circ\text{C}$ ) [41], the phenol will mainly exist as neutral species when pH value is less than the  $pK_a$ , while it will be negatively

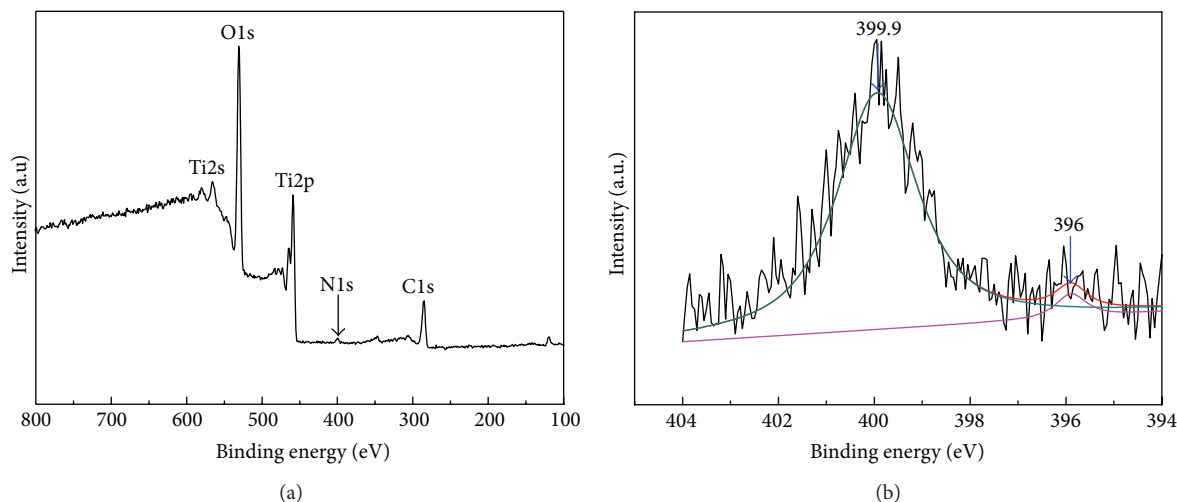


FIGURE 4: XPS survey spectra of (a) survey spectrum and (b) N1s.

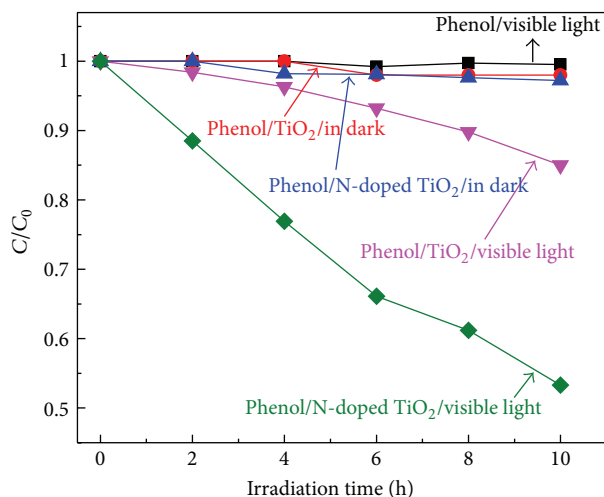


FIGURE 5: Photodegradation of phenol with 0.25 g catalysts at pH = 6 under different conditions.

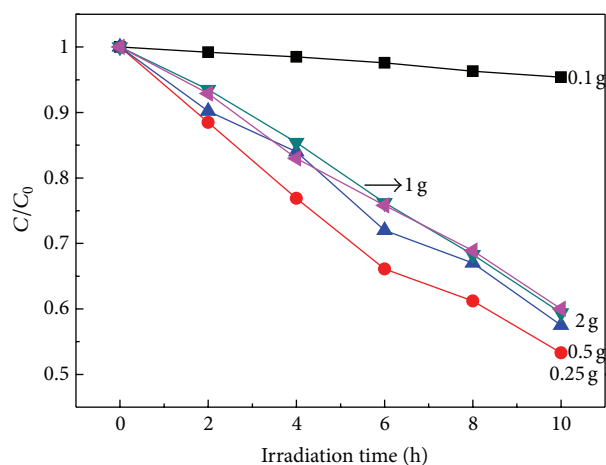


FIGURE 6: Effects of N-doped TiO<sub>2</sub> powders load on the photodegradation of phenol at pH = 6.

charged when the pH is larger than the  $pK_a$ . That is, phenol molecules can be scarcely adsorbed on the surface of N-doped TiO<sub>2</sub> particles due to the columbic repulsion between them as the surface of N-doped TiO<sub>2</sub> particles and phenol molecules are both negatively charged when pH = 10. Therefore, very little phenol could be decomposed. At the case when pH < 10, phenol is primarily presented in neutral molecular form while the surface of TiO<sub>2</sub> particles are positively (or negatively when pH > 6.4) charged. The electrostatic attraction between TiO<sub>2</sub> particles and phenol molecule increases the amount of adsorbed phenol and then enhances the photodegradation. Besides, agglomeration has also been considered as one of the key factors that affect the photocatalytic activity. When the pH is relatively low, large repulsive forces between the TiO<sub>2</sub> particles may occur due to the positive charges caused by the reaction (1); thus, the dispersion of the TiO<sub>2</sub> particles in the suspension could be improved and the photocatalytic performance could be enhanced as well due to the decreased agglomeration of the particles. Therefore, the better photodegradation occurs at the case when pH value is 4.

The photodegradation of phenol is complex and may produce complex intermediates such as toxic aromatic intermediates as reported in many researches [42, 43]. Generally, phenol is firstly oxidized to aromatic intermediates such as hydroquinone, catechol, benzoquinone, and 4, 4'-dihydroxybiphenyl, and then phenyl rings of these aromatic intermediates break up to form aliphatic acid which is further oxidized to short-chain organic acid such as oxalic acid, acetic acid, and formic acid. Finally, they are decomposed to carbon dioxide and water completely [11, 37]. The aromatic intermediates always have colors. For example, the color of the mixture of catechol and hydroquinone aqueous solution is pink, while that of m-dihydroxybenzene and benzoquinone are yellow and brown, respectively [44]. The absorption peaks corresponding to aromatic intermediates and ring cleavage products have been detected in the UV-Vis absorption spectra of phenol degradation by researchers [45, 46]. However,

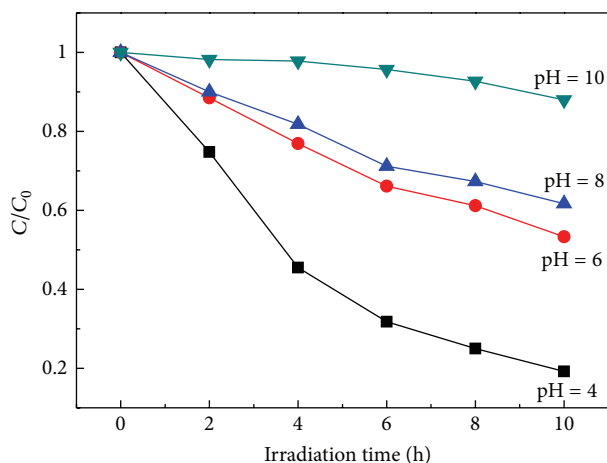


FIGURE 7: Effect of pH value on the photodegradation of phenol with 0.25 g N-TiO<sub>2</sub> powders.

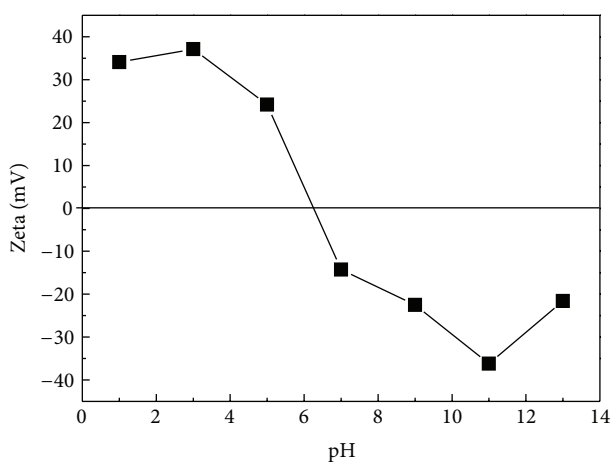


FIGURE 8: Zeta potential of N-doped TiO<sub>2</sub> powders in phenol aqueous solution at different pH values.

in our experiments, the solution after photodegradation is colorless, and no clear absorption peaks corresponding to aromatic intermediates and ring cleavage products are detected in the spectra, as shown in Figure 9, which indicates that there is little photodegradation intermediates produced in the photodegradation of phenol process and the good photocatalytic performance of our samples.

#### 4. Conclusion

N-doped TiO<sub>2</sub> was successfully synthesized by a mild hydrothermal method at 150°C and holding for 2 h without any postheat treatment for crystallization. The grain size of the powders was about 10 nm, and the specific surface area of N-doped TiO<sub>2</sub> was 154.7 m<sup>2</sup>/g. The absorption edge of N-doped TiO<sub>2</sub> had been shifted to 420 nm, and the band energy was about 2.90 eV estimated by Kubelka-Munk function after nitrogen doping. Nitrogen atoms have been successfully incorporated into the lattice of TiO<sub>2</sub>. The amount of catalyst

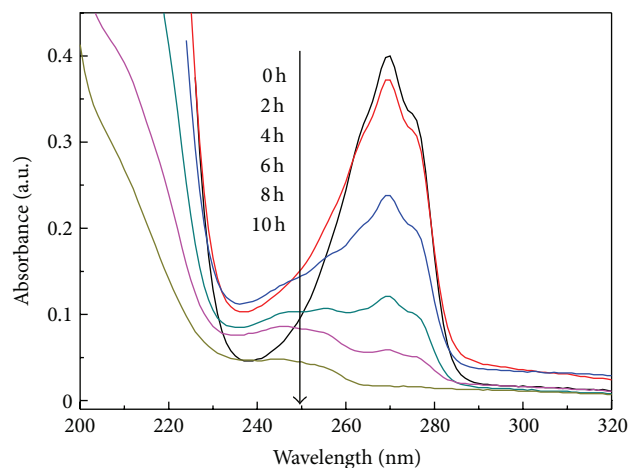


FIGURE 9: UV-Vis absorption spectra of phenol degradation with 0.25 g N-doped TiO<sub>2</sub> at pH 4.

and pH value was optimized as 0.25 g and 4, respectively, for better photocatalytic performance in our experiment conditions. The photodegradation reached 81% after 10 h of visible light irradiation.

#### Acknowledgments

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