

# Surface modification of nanometer size TiO<sub>2</sub> with salicylic acid for photocatalytic degradation of 4-nitrophenol

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Received 30 July 2005; received in revised form 31 October 2005; accepted 7 December 2005

Available online 19 January 2006

## Abstract

The efficiency of photocatalytic reactions was limited by the wide band-gap of TiO<sub>2</sub> and the high degree of electron–hole recombination inherent in photocatalytic process, as well as by the limited adsorption capability of photocatalysts. In order to increase the overall efficiency, the surface of nanometer size TiO<sub>2</sub> was simply and fast modified by chemical adsorption in saturated solution of salicylic acid. A stable, light yellow surface complex was formed quickly, which has obvious absorption in the region from 320 to 420 nm. Through surface modification, the adsorption efficiency of 4-nitrophenol by TiO<sub>2</sub> was enhanced from 42 to 84%. The photocatalytic efficiency was tested on the degradation of 4-nitrophenol. The influences of catalyst and its dosage, pH value, and 4-nitrophenol concentration on the degradation were investigated. Under such photodegradation conditions as initial pH 4.0, 4-nitrophenol 5 mg l<sup>-1</sup>, catalyst 100 mg, and irradiation time 160 min with 160 W high-pressure mercury lamp, the degradation efficiency of 4-nitrophenol by TiO<sub>2</sub> was increased from 39.5 to 79.3% after surface modification, and furthermore, the degradation efficiency could be enhanced to 91.1% if the concentration of 4-nitrophenol was not more than 1 mg l<sup>-1</sup>. Compared with the pure TiO<sub>2</sub>, surface modification led not only to improve the surface coverage of 4-nitrophenol, but also to increase the light utilization. Both of these factors were crucial for the photocatalytic activity of heterogeneous photocatalysis, especially for photodegradation of aromatic pollutants.

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**Keywords:** Titanium dioxide; Surface modification; Salicylic acid; Nitrophenol; Photocatalysis

## 1. Introduction

Nitroaromatic compounds are of environmental concern because they are widely used as herbicides, explosives, solvents and industrial chemicals or precursors [1]. Widespread use of these compounds has led to contamination of soils, waste streams and surface waters. Nitroaromatic compounds exhibit high toxicity and/or mutagenicity for many living organisms either directly or through some of their catabolic metabolites [2]. Nitrophenols are on the list of United States Environmental Protection Agency as priority pollutants [3].

Photocatalytic degradation is an efficient and economic method to decompose nitrophenols into less dangerous materials. Nitrophenols have been catalytically degraded by CuO [4,5] or TiO<sub>2</sub> [6,7]. TiO<sub>2</sub> as a photocatalyst has band-gaps of approximately 3.0–3.2 eV, the photocatalytic process must be induced

by UV light irradiation. The extreme low surface coverage of organic pollutants on the catalyst TiO<sub>2</sub> is the key factor that has resulted in the low photocatalytic efficiency [6,8]. Thus, recent studies are focused on the modification of TiO<sub>2</sub>, including activated carbon coating [9], transition metal doping [10–12], metal ion implanting [13], surface derivating with Fe(III)-porphyrin [14] or ascorbic acid [15] or polymer [16]. Above mentioned modification methods are time-consuming, high cost, and complicated, for example, TiO<sub>2</sub> must be heated under reflux in a nitrogen atmosphere for 84 h for the synthesis of the *N,N*-dialkyl-4,4-bipyridinium-modified titanium-dioxide [16]; and furthermore, the surface coverage of organic pollutants on the catalyst TiO<sub>2</sub> is still poor.

Aromatic compounds are common pollutants, especially as priority pollutants, and difficult to degradation in environment. The affinity between the catalyst TiO<sub>2</sub> and pollutants is an important factor in enhancing the photodegradation efficiency. So aromatic carboxylic acid, such as benzoic acid, and salicylic acid is used as surface modifiers for five purposes: (a) to enhance the surface coverage of aromatic pollutants on TiO<sub>2</sub> by phenyl

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group interaction; (b) to develop a simply and fast surface modified technology, using chemical adsorption by  $\text{TiO}_2$  through an ester-like bond between  $-\text{COOH}$  group and the surface  $-\text{OH}$  groups of  $\text{TiO}_2$ ; (c) to improve the dispersive capacity of catalyst  $\text{TiO}_2$  powder in polar and non-polar solvent by hydrophilic group  $-\text{COOH}$ ,  $-\text{OH}$ , and hydrophobic group  $-\text{phenyl}$ ; (d) to accelerate the migration rate of pollutant to the surface of  $\text{TiO}_2$ ; (e) to expand the wavelength response range. Such factors, we thought, were crucial for the photocatalytic activity of heterogeneous photocatalysis.

## 2. Experimental

### 2.1. Materials

Nanometer size  $\text{TiO}_2$  (anatase, its diameter was 10–30 nm) was provided by the laboratory of Inorganic Chemistry, Department of Chemistry, Wuhan University. Its synthesis method and character of the nanometer size  $\text{TiO}_2$  were described in Ref. [17]. 4-Nitrophenol was purchased from Eastman Kodak Co. (Rochester, New York). Benzoic acid (BA) and salicylic acid (SA) were obtained from Sigma Chemical Co. (St. Louis, Missouri), its saturated solutions were prepared and used at once, in order to avoid oxidation by dissolved oxygen. All other chemicals were of analytical grade. Doubly distilled deionized water was used throughout the experiment. UV–vis scanning spectrophotometer (Perkin-Elmer Lambda 900), 320-S pH meter (Mettler-Toledo Delta), high-pressure mercury lamp (160 W), HJ-3 constant temperature stirrer by magnetic force, and SYZ-B quartz double distilled deionized distillatory were used.

### 2.2. Surface modification

Surface modification was carried out through stirring the nanoparticles  $\text{TiO}_2$  for 30 min in the saturated solution of BA and SA, respectively, resulting in a light yellow colouration of the surface of  $\text{TiO}_2$  modified by SA. After filtered with 0.45  $\mu\text{m}$  membrane filter, the modified  $\text{TiO}_2$  ( $\text{TiO}_2$ -BA and  $\text{TiO}_2$ -SA) was washed with water three times, heat-treated for 30 min at 105 °C. It was worth noting that the colour developed imminently, implying that a chemical reaction took place (chemisorption) between SA (surface modifier) and  $\text{TiO}_2$ .

### 2.3. Determination of 4-nitrophenol

The concentration of 4-nitrophenol was measured by a UV spectrophotometer. After illumination, clear samples were obtained by filtering the solution using Millipore filter (0.45  $\mu\text{m}$ ), then pH was adjusted to 9.0 and they were used for the analysis of 4-nitrophenol by measuring the absorbance at 400 nm.

### 2.4. Photocatalytic degradation experiment

A cylindrical Pyrex photoreactor was used, inside which a 160 W high-pressure mercury lamp was positioned, its vessel

was surrounded by a circulating water jacket (Pyrex) to cool the reaction solution. Prior to irradiation, after adjusting pH, the suspensions (100 ml, including 100 mg photocatalyst) were magnetically stirred in the dark for 150 min to establish the adsorption/desorption equilibrium of 4-nitrophenol. The aqueous suspensions containing 4-nitrophenol were irradiated with constant aerating. At given irradiation time intervals, samples were taken from the suspension, then passed through a 0.45  $\mu\text{m}$  Millipore filter to remove the particles, the concentration of 4-nitrophenol in the filtrate was determined at once.

### 2.5. Characterization of photocatalyst

To determine the wavelength response range, UV–vis absorption spectra were obtained in the range of 200–550 nm. To investigate the dispersive capacity of photocatalyst in polar and non-polar solvent, dispersal and sedimentation experiment was observed as follow: 100 mg of nanoparticles ( $\text{TiO}_2$  or  $\text{TiO}_2$ -SA) was added into 100 ml solution of water, benzene and ethanol, respectively; the suspension was stirred for 30 min, and then kept standing. The affinity interaction between aromatic pollutant and photocatalyst was tested with the adsorption experiment. After adjusting pH 4.0, the suspensions (100 ml, including 100 mg photocatalyst) were magnetically stirred in the dark for time intervals, samples were taken from the suspension, then passed through a 0.45  $\mu\text{m}$  Millipore filter to remove the particles, the concentration of 4-nitrophenol in the filtrate was determined at once.

## 3. Results and discussion

### 3.1. Influence of surface modification on the wavelength response range

Benzoic acid and salicylic acid do not absorb any light above 300 nm, and  $\text{TiO}_2$  absorbs light of wavelengths <380–400 nm. Following surface modification, the formation of  $\text{Ti}^{\text{IV}}$ -SA surface complex results in a shift of the absorption threshold, towards the visible region of the spectrum, up to 420 nm, then the utilization of light from high-pressure mercury lamp was enhanced. The photoemission spectrum of mercury lamp, and the UV–vis spectra of the  $\text{TiO}_2$  and its derivatives, were illustrated in Figs. 1 and 2.

The appearance of light yellow colour on the  $\text{TiO}_2$  powder modified with SA could be explained as a result of an intense

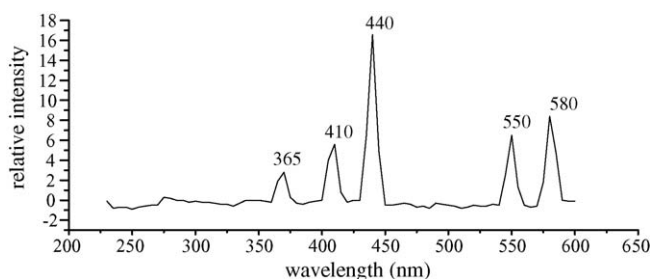


Fig. 1. The emission spectrum of the high-pressure mercury lamp.

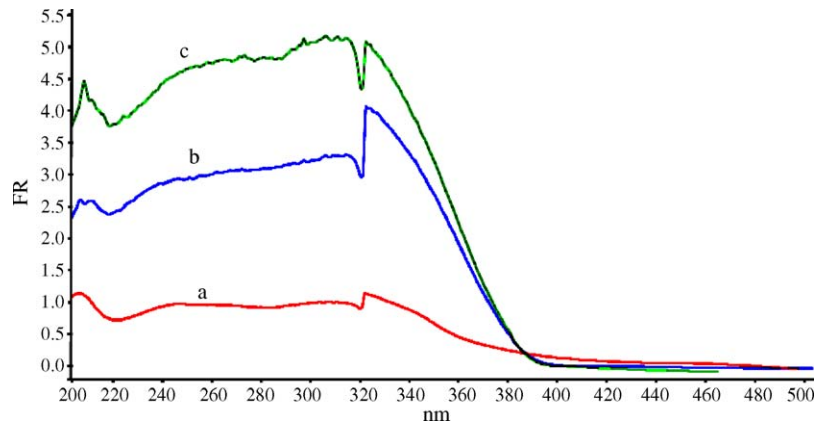


Fig. 2. UV-vis absorption spectra of the  $\text{TiO}_2$  and its surface modified derivatives. (a) Salicylic acid-modified  $\text{TiO}_2$ ; (b) benzoic acid-modified  $\text{TiO}_2$ ; (c)  $\text{TiO}_2$ .

ligand to metal charge transfer transition. It was well known that titanium ions readily form complexes with oxygen atoms from various oxygen-containing ligands. Small particle colloids present an increased surface to bulk ratio, and therefore, possess a significant number of unsaturated metal atoms (for a 30 nm colloid  $\text{TiO}_2$  about 50% of titanium atoms are located at the particle surface) [13], very active chemically and capable of forming chelate complexes. Further evidence for the formation of such a complex was obtained by the reaction of SA with titanium ions. Addition of SA in an ethanolic solution of titanium isopropoxide leads to the evolution of a yellow colour cloudy precipitate, with a spectrum similar to the SA modified  $\text{TiO}_2$

surface. Consequently, one could claim that SA interacts with the nanometer size  $\text{TiO}_2$  surface in a manner that parallels solution chemistry.

This hypothesis (Fig. 3) was confirmed by the infrared spectrum (Fig. 4) of the modified  $\text{TiO}_2$  nanoparticles. The absorption peaks from  $-\text{OH}$  groups ( $3182\text{--}3213\text{ cm}^{-1}$ ,  $\text{TiO}_2$  surface), phenyl ( $1441$  and  $1477\text{ cm}^{-1}$ ) and  $-\text{COOTi}-$  group ( $1385\text{ cm}^{-1}$ ) were observed on SA derivatised  $\text{TiO}_2$  surface. According to UV-vis spectra and infrared spectrum, the interaction between  $\text{TiO}_2$  and BA was weak. The formation of ester with stable six-member ring could avail the esterification between salicylic acid and  $-\text{OH}$  groups on  $\text{TiO}_2$  surface, but such reaction

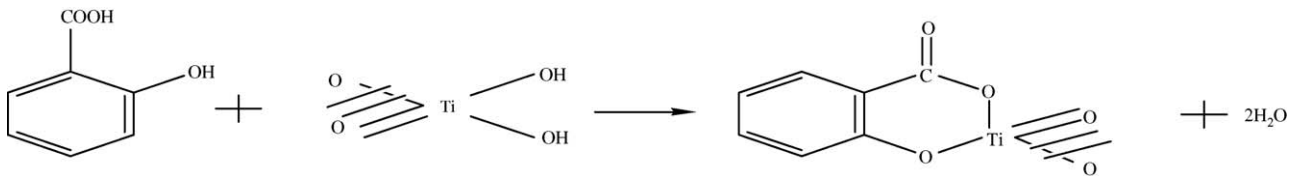


Fig. 3. Hypothetic esterification between salicylic acid and  $-\text{OH}$  groups on  $\text{TiO}_2$  surface.

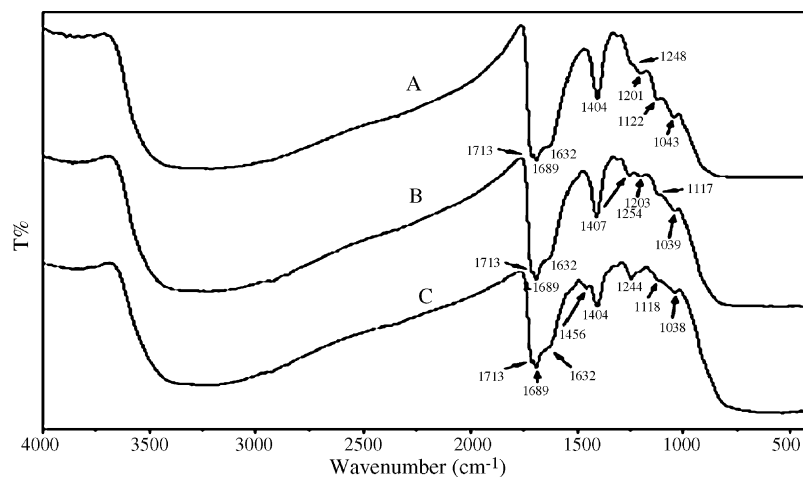


Fig. 4. Infrared spectrum of the modified  $\text{TiO}_2$  nanoparticles. (A)  $\text{TiO}_2$ ; (B) benzoic acid-modified  $\text{TiO}_2$ ; (C) salicylic acid-modified  $\text{TiO}_2$ .

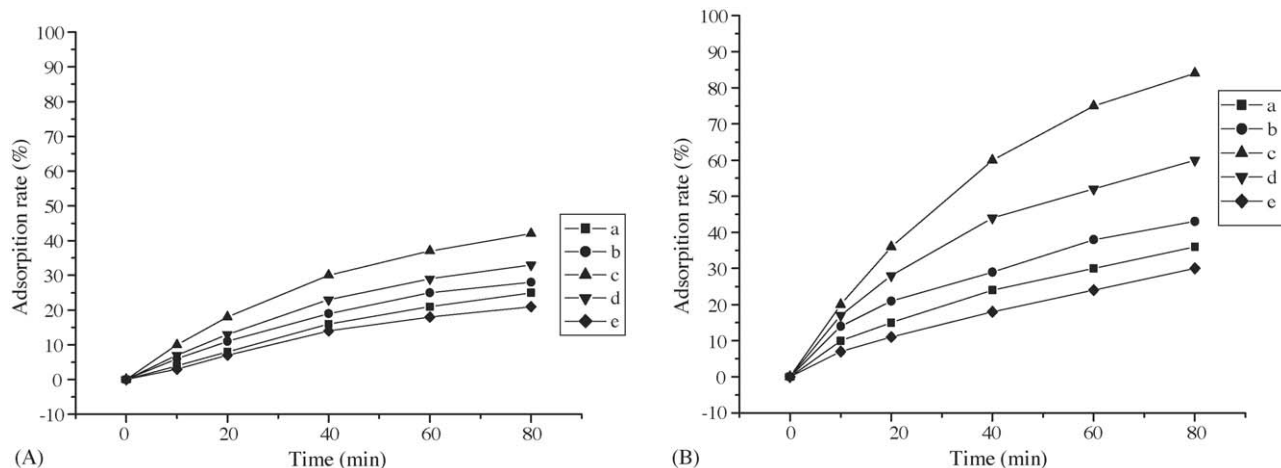


Fig. 5. Effect of pH on the adsorption of 4-nitrophenol on TiO<sub>2</sub> nanoparticles and its modified derivative. (A) TiO<sub>2</sub>; (B) salicylic acid-modified TiO<sub>2</sub>; (a) pH 1; (b) pH 2; (c) pH 4; (d) pH 5; (e) pH 6.

could not proceed if salicylic acid was replaced by benzoic acid.

### 3.2. Influences of surface modification and pH on the adsorption capability

The surface coverage of organic pollutants on the catalyst TiO<sub>2</sub> was the key factor that dominated the photocatalytic efficiency of heterogeneous photocatalysis. The effects of surface modification with salicylic acid and the pH value of the suspension on the adsorption capability of 4-nitrophenol are shown in Fig. 5.

This adsorption capability was greatly affected by the pH value, and its effect on TiO<sub>2</sub> and TiO<sub>2</sub>-SA was quite similar. The optimum pH value for adsorption of 4-nitrophenol by TiO<sub>2</sub> and TiO<sub>2</sub>-SA was the same, i.e., 4.0. Through surface modification with SA, the adsorption efficiency of 4-nitrophenol by TiO<sub>2</sub> was enhanced from 42 to 84%, the surface coverage of aromatic pollutants on TiO<sub>2</sub> was enhanced two times by phenyl group interaction.

### 3.3. Influence of surface modification on the degradation efficiency

Under the irradiation with high-pressure mercury lamp, photocatalytic degradation of 4-nitrophenol could be induced by TiO<sub>2</sub> and TiO<sub>2</sub>-SA. After irradiation for 160 min, the maximal degradation efficiency of 39.5% for TiO<sub>2</sub> and 79.3% for TiO<sub>2</sub>-SA were deduced from Fig. 6.

The degradation efficiency has been improved two times. Through surface modification with SA, the photocatalytic activity of TiO<sub>2</sub> was improved significantly; it was due to three factors (a) the enhancement of surface coverage of 4-nitrophenol on the catalyst; (b) accelerating the migration rate of 4-nitrophenol to the surface of the catalyst; (c) expanding the wavelength response range; the first factor, we thought, is the key contributor because the increased times of the adsorption efficiency and the degradation efficiency was quite close.

The complex of TiO<sub>2</sub>-SA was irradiated directly 240 min by high-pressure mercury lamp, then it was used for photocatalytic degradation of 4-nitrophenol. Its colouration was kept light yellow; the photodegradation efficiency was still 79.3%; so, the complex of TiO<sub>2</sub>-SA was stable during photocatalytic degradation experiment.

### 3.4. Influence of pH, mass of salicylic acid-modified TiO<sub>2</sub>, and concentration of 4-nitrophenol on the degradation efficiency

Fig. 7 indicates the effect of pH on the degradation efficiency of 4-nitrophenol by salicylic acid-modified TiO<sub>2</sub>. The influence of pH values such as 2, 3 and 5, on the degradation and adsorption was different. The optimum pH value for the photodegradation of 4-nitrophenol was 4.0, and it is same for the adsorption of 4-nitrophenol. It is proved once again that surface coverage of organic pollutants on the catalyst was crucial for the photocatalytic activity of heterogeneous photocatalysis.

In order to get the acceptable mass of salicylic acid-modified TiO<sub>2</sub> for the photodegradation of 4-nitrophenol, 50, 100, 150, 200 and 250 mg of TiO<sub>2</sub>-SA were added to 100 ml suspensions

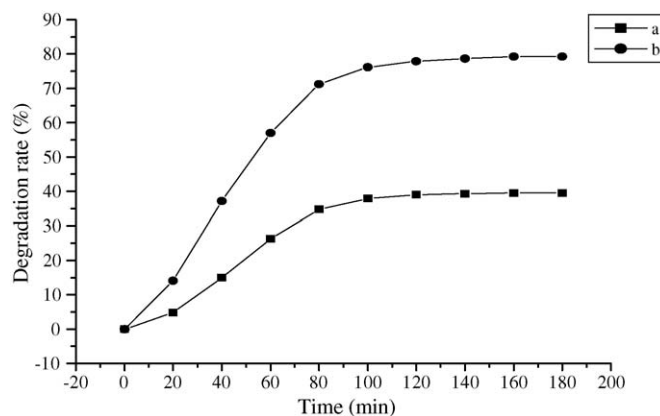


Fig. 6. Effect of surface modification on the degradation efficiency of 4-nitrophenol (5 mg l<sup>-1</sup>). (a) TiO<sub>2</sub> and (b) salicylic acid-modified TiO<sub>2</sub>.

Table 1

Effect of mass of salicylic acid-modified TiO<sub>2</sub> (concentration: 5 mg l<sup>-1</sup>) and concentration of 4-nitrophenol on the degradation efficiency (mass: 100 mg)

	Mass of salicylic acid-modified TiO <sub>2</sub> (mg)					Concentration of 4-nitrophenol (mg l <sup>-1</sup> )				
	50	100	150	200	250	1	2	3	4	5
Degradation efficiency (%)	69.9	79.3	60.4	55.7	50	91.1	84.9	82.3	79.6	79.3

containing 5 mg l<sup>-1</sup> 4-nitrophenol, stirred and irradiated for 160 min. The samples were taken from the suspension, passed through a 0.45 μm Millipore filter to remove the particles, the concentration of 4-nitrophenol in the filtrate was determined at once. The influences of the mass of TiO<sub>2</sub>-SA on the degradation efficiency of 4-nitrophenol were shown in Table 1.

The optimum mass of TiO<sub>2</sub>-SA was 100 mg in 100 ml suspension, i.e., 1 mg ml<sup>-1</sup>. TiO<sub>2</sub>-SA was used as adsorbent and photocatalyst in this photochemical reaction system; when its dosage was less than 100 mg, the adsorption and degradation of 4-nitrophenol was limited for its shortage; when its dosage was over 100 mg, its adsorption capability was enhanced, but the absorption of light by the photocatalyst was also obstructed greatly for its interception and scattering of light, photocatalytic reaction could not be taken place without light-induction, the photocatalytic efficiency was depressed. The photocatalytic degradation efficiency was greatly affected by the concentration of 4-nitrophenol because the dose of TiO<sub>2</sub>-SA was limited to no more than 1 mg ml<sup>-1</sup>, the active spots of adsorption and photocatalysis were limited too. When the concentration of 4-nitrophenol is not more than 1 mg l<sup>-1</sup>, the degradation efficiency could be enhanced to 91.1%. Unfortunately, due to the limit of the dose, nanometer size particle of TiO<sub>2</sub>-SA could be used for the degradation of high concentration of 4-nitrophenol. However, this shortcoming, we thought, could be overcome by immobilization technology, for example the TiO<sub>2</sub> films; because the effects of the interception and scattering of light from the catalyst/adsorbent could be reduced, the dose of TiO<sub>2</sub>-SA, and its active spots of adsorption and photocatalysis could

be increased to extend the valid degradation concentration of 4-nitrophenol.

### 3.5. Influence of the reuse of salicylic acid-modified TiO<sub>2</sub> catalyst on the degradation efficiency

Hundred milligrams TiO<sub>2</sub>-SA catalyst was reused six times to degrade 100 ml 1 mg l<sup>-1</sup> 4-nitrophenol, washing the catalyst with water after each use, putting a new portion of 4-nitrophenol, and repeating the repetitive experiments. The results were similar as shown in Fig. 7c, but the degradation efficiency was decreased slightly from 91.1 to 87.5% for the unavoidable losing of TiO<sub>2</sub>-SA during the wash. Such repetitive experiments also proved that TiO<sub>2</sub>-SA was a true and photo-stable photocatalyst, and not a complex that could decompose after under light.

## 4. Conclusions

The surface of nanometer size TiO<sub>2</sub> could be simply and fast modified by chemical adsorption in saturated solution of salicylic acid. After surface modification, the wavelength response range of TiO<sub>2</sub> was expanded, it has obvious absorption in the region from 320 to 420 nm; the adsorption efficiency of 4-nitrophenol was enhanced from 42 to 84%. Under optimal photodegradation conditions, including initial pH 4.0, 4-nitrophenol 5 mg l<sup>-1</sup>, catalyst 100 mg, irradiation time 160 min with 160 W high-pressure mercury lamp, the degradation efficiency of 4-nitrophenol by TiO<sub>2</sub> was increased from 39.5 to 79.3% after surface modification, and furthermore, the degradation efficiency could be enhanced to 91.1% if the concentration of 4-nitrophenol was not more than 1 mg l<sup>-1</sup>. Surface modification led not only to an increase in the light utilization, but also improved the surface coverage of 4-nitrophenol in comparison with the pure TiO<sub>2</sub>. Both of these factors are crucial for the photocatalytic activity of heterogeneous photocatalysis, especially for photodegradation of aromatic pollutants.

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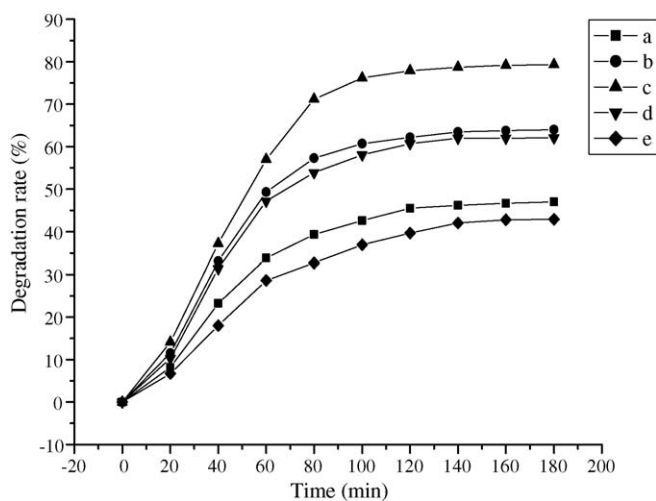


Fig. 7. Effect of pH on the degradation efficiency of 4-nitrophenol (5 mg l<sup>-1</sup>) by salicylic acid-modified TiO<sub>2</sub>. (a) pH 2; (b) pH 3; (c) pH 4; (d) pH 5; (e) pH 6.

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