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Doping of TiO_2 with nitrogen to modify the interval of photocatalytic activation towards visible radiation

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Abstract

A simple method for the doping of titanium dioxide with nitrogen was developed. By this technique, commercial titanium dioxide was thermally treated under a nitrogen enriched atmosphere. The N doped TiO_2 presented a slight displacement in the absorption edge of light, towards the visible radiation range. Phenol degradation in water solution was used to compare photocatalytic activity of doped titania. With the treatment at 600 °C, the photocatalitic activity of the N–TiO_2 was improved, and the changes of anatase to rutile phases ratio as well as specific surface area were minimal. The higher activity obtained after TiO_2 treatment could be correlated with the modification in radiation absorption spectra, since the radiation used for the determination of the photocatalytic activity was in the edge of the UV–vis radiation. Treatments at higher temperature shown almost the same activity of undoped titania, but sintering reduced the surface area per gram of TiO_2, thus the photocatalytic activity of doped surface was more active (moles of phenol transformed/m^2 h).

Keywords: Photocatalysis; Titanium dioxide; Visible light

1. Introduction

The photocatalytic degradation of several diluted toxic compounds in water using UV radiation and TiO_2 as photocatalyst has been widely studied by several authors. The great interest on this reaction is due to the high impact that would have the development of a technology for degradation of low concentration pollutants in water at room temperature [1]. Among several photocatalysts, TiO_2 is ideal due to its high chemical stability, high photocatalytic activity to oxidize pollutants from air and water and in addition, TiO_2 is not toxic [2]. Nevertheless, TiO_2 is only activated under UV radiation, and this limits its application significantly [3]. The UV radiation sources have a high cost, and of the solar spectrum of radiation that reaches the terrestrial surface, less than 5% corresponds to UV radiation [4].

Therefore, an effort is necessary to develop a low cost photocatalyst to work not only under UV radiation, but also under visible radiation range, i.e. photocatalyst must be able to generate the electron–hole pair under visible radiation to start the oxidation of organic compounds at photocatalyst surface [1].

Several works have been reported indicating that the doping of TiO_2 with some transition metals extend the edge of radiation absorption towards the visible region, and an improvement on photocatalytic properties of TiO_2 is obtained [5,6]. Other authors report that the doping of TiO_2 structure with non-metallic elements, like sulphur and nitrogen, produces the same effect, i.e. the extension of the absorption edge towards visible radiation [3]. According to Asahi et al. [7], the doping of TiO_2 with nitrogen, lead to a narrowing in the bad gap due to the mixing of p states of nitrogen with O 2p from oxygen.

Some works report the doping of TiO_2 with nitrogen, like the synthesis of $TiO_{2-x}N_x$ films by sputtering of TiO_2 precursor under a nitrogen/argon gas mixture [7]. Another

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reported method consists of warming up dusts of anatase TiO_2 up to 600 °C in an atmosphere of a gas mixture of ammonia and argon, or by oxidation of titanium nitrate at temperatures between 400 and 550 °C [8]. Burda et al. [9] reported the synthesis of nanoparticles doped with nitrogen, which is an expensive method to insert nitrogen, since N–TiO_2 is obtained from titanium(IV) isopropoxide hydrolysis. The object of this work is to dope nitrogen on TiO_2 photocatalyst, using a low cost process.

2. Experimental

2.1. Preparation of photocatalysts

Nitrogen doped TiO_2 was prepared by the thermal treatment of TiO_2 Degussa P-25, in a dynamic system using ammonium hydroxide as nitrogen source. Fig. 1 shows the diagram of the doping system. Ammonia solution from J.T. Baker (~25% in water) was nebulized using Hospitak nebulizer, Model HK 950 into reaction chamber using air flow at 2 l/min as carrier. Simultaneously a TiO_2 water suspension containing 10% of TiO_2 was fed as small drops into the vertical quartz tube by means of a peristaltic pump. TiO_2 particles attached to the tube walls and formed agglomerates which then felt down to the collector. The aim of this treatment was to expose the surface of TiO_2 particles to an ammonium rich atmosphere at high temperature in order to substitute some oxygen atoms by atoms of nitrogen. Temperature treatment was 600, 700 and 800 °C, and nomenclature of samples indicate the temperature at which nitrogen doping was made.

2.2. Characterization of photocatalysts

The UV–vis spectra were obtained using a Perkin-Elmer spectrometer, Model Lambda 10 with magnesium oxide being used as reference. The X-ray diffraction patterns were obtained in a Siemens X-ray Diffractometer Model D5000 and the 2θ angle was scanned from 5 to 80. Surface area measurements were made by nitrogen adsorption in Autosorb-1C equipment from Quantachrome.

2.3. Photocatalytic activity tests

Photocatalytic activity evaluation was carried out via the degradation of phenol in water solution. Five millilitres of 100 ppm phenol in water were placed in a petri dish with 0.5 g of photocatalyst, which allows the dispersion of all the photocatalyst in the bottom of dish; therefore, minimizing the existence of non-exposed particles. Since phenol quantification requires water sampling and the TiO_2 particle size is very low and can be introduced into sampling syringe, photocatalyst powders were pressed to obtain a disk. The disks were later broken to obtain small bits of photocatalyst and sieved to select grains between 0.707 and 0.297 mm, with this procedure we avoid the loss of TiO_2 powder during sampling for chromatographic analysis. The petri dishes were covered by thermal adjustable polyethylene film to avoid the evaporation of water and phenol; condensed drops from solution on the film were not observed during reaction test. The phenol concentration change was determined by a Perkin-Elmer Autosystem gas chromatograph. The activity tests were made with UV–vis lamp of low energy, which has a radiation distribution centered in 360 nm wavelength. Radiation intensity was measured with three radiometers and the

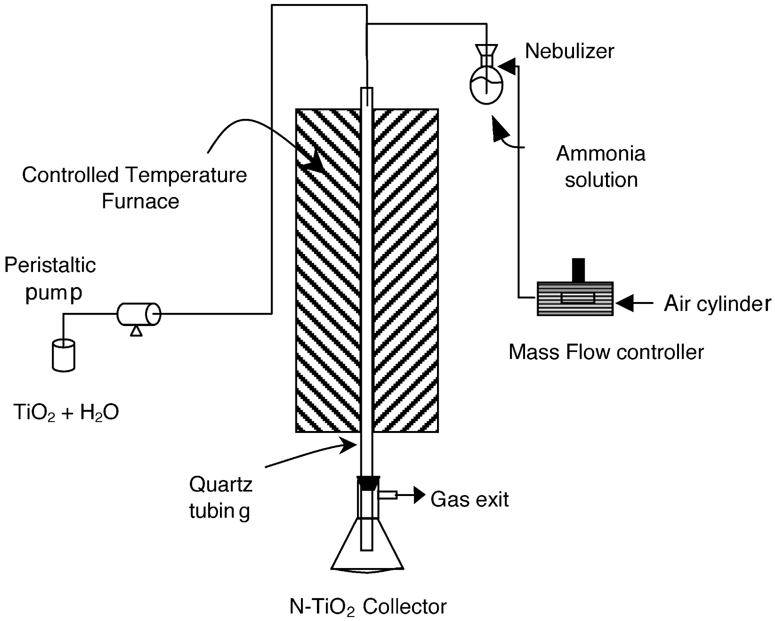

Fig. 1. Schematic diagram of doping system.

following radiation intensities were obtained: for radiometer of high energy, with wavelength of 210 nm, intensity was 80 μW/cm^2; for radiometer at 310 nm, 490 μW/cm^2; for 360 nm, the measured intensity was 1620 μW/cm^2. Considering that lamp wavelength distribution approximates to normal distribution, according to the measured radiation intensities, the lamp also emits visible radiation, (~650 μW/cm^2 at 400 nm). The determination of photocatalytic activity of doped TiO_2 was always made simultaneously with the TiO_2 Degussa P25 as reference, i.e. reactor charged with N–TiO_2 and reactor with P25 were placed under the same lamp at the same time and conversion on both reactions was followed by chromatographic analysis. This procedure minimizes the experimental error. Less than 5 μl of water sample were taken for each chromatographic analysis, which corresponds to less than 0.1% of water at reactor, thus overall photodegradation rate is not affected by reaction volume change.

3. Results and discussion

3.1. Characterization

The samples post nitrogen doping treatment showed a slight change of color to yellowish, resembling the color that is observed when a change of phase from anatase to rutile is obtained at high temperatures. This slight yellowish color was also reported for nitrogen doped TiO_2 prepared by hydrolysis of several precursors [8]. The XRD measurements show that anatase is the main phase. As is well known, TiO_2 Degussa P25 consists of an 80% anatase and 20% rutile and as can be seen in Fig. 2, there is no significant change in anatase to rutile ratio for nitrogen doped TiO_2 at 600 °C. The differences between untreated P25 and treated P25 start to be noticeable for treatments at 700 and 800 °C where the phase ratio of main peaks, anatase (1 0 1)/rutile (1 1 0), decreases.

The results obtained for surface area analysis are shown in Table 1, and as can be seen, change of surface area is negligible for sample treated at 600 °C and reduction of surface area becomes important for samples treated at 700 and 800 °C. Considering that TiO_2 Degussa P25 is a non-porous material which consists of spherical particles with a mean diameter of 30 nm, the loss of surface area must be due to sintering of the nanoparticles. There is no significant difference between sample P25 and N–TiO_2 600 in surface area, and the reported values at Table 1 are equivalent, since the difference is within the analytical error of the equipment.

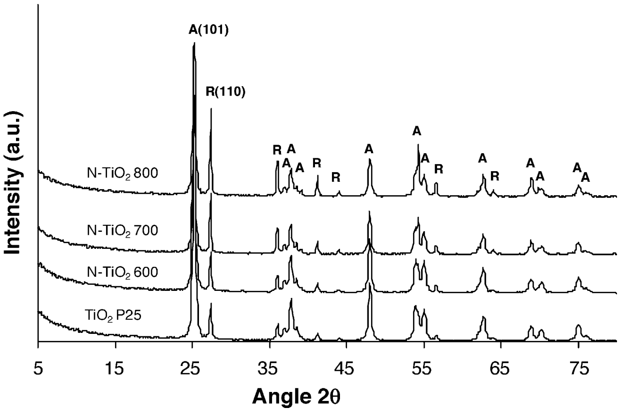

Fig. 2. XRD patterns of photocatalysts, peaks identified correspond to anatase (A) or rutile (R) phases.

Table 1
Specific surface area and band gap energy of photocatalysts

Sample	Surface area (m^2/g)	Band gap energy (eV)
TiO_2 P25	49	3.01
N–TiO_2 600	51	2.93
N–TiO_2 700	43	2.97
N–TiO_2 800	30	2.88

The result of the analysis of UV–vis absorption by diffuse reflectance is shown in Fig. 3. As can be observed, a slight displacement of the absorption of radiation exists towards the visible frequency for the three samples doped with nitrogen. This result corroborates that the treatment induces a modification of the structure of the TiO_2. Based on the way that treatment is made, this change not necessarily represents the bulk change in the oxide, but a modification on the surface.

Appling the Kubelka–Munk model, the determination of band gap was calculated for the all the samples, as shown in Table 1. According to these calculations, the change of band gap is lower than 0.15 eV for the method here reported to insert nitrogen atoms in TiO_2 structure, which is higher than the change reported by Sakthivel and Kisch [8] for samples

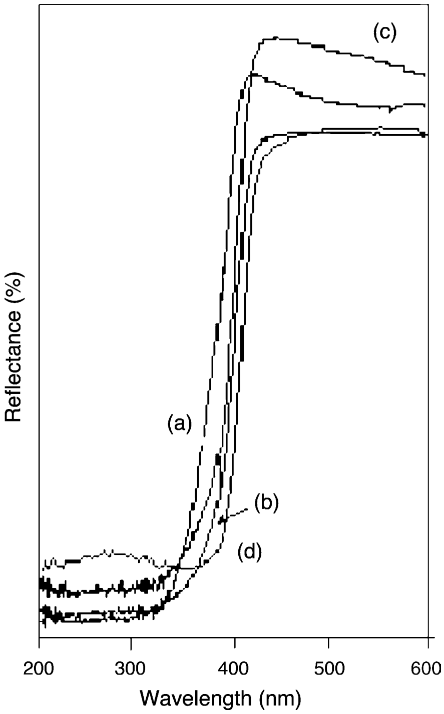

Fig. 3. The diffuse reflectance UV–vis spectra of photocatalysts: (a) TiO_2 P25; (b) N–TiO_2 600; (c) N–TiO_2 700; (d) N–TiO_2 800.

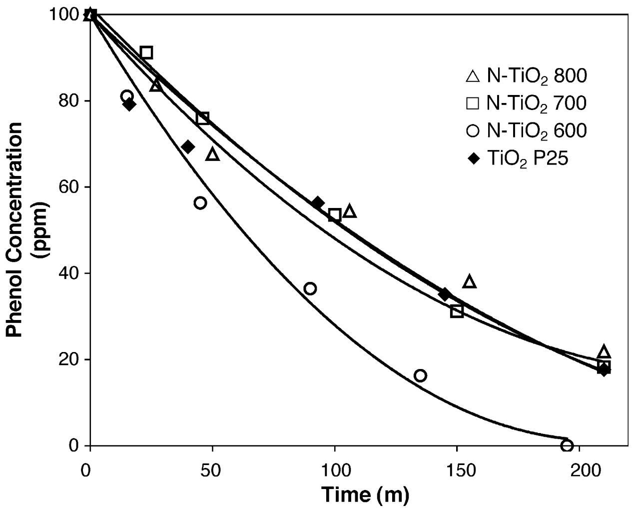

Fig. 4. Photocatalytic phenol degradation by the nitrogen doped TiO_2 and unmodified TiO_2 Degussa P25.

prepared by hydrolysis and calcination, but lower than the obtained by Miao et al. [3] for thin films.

3.2. Photocatalytic activity

Fig. 4 shows the results of photocatalytic degradation of phenol water solution. As can be seen, best results were obtained for sample treated at 600 °C, no improvement is observed for samples treated at 700 and 800 °C.

One of the main problems associated to high temperature thermal treatment of photocatalysts is that dehydroxylation of surface reduced the activity, and before this work were made, we speculated that surface dehydroxylation could be a problem, after nitrogen insertion in titania structure by our method. Nevertheless, surface was not severely affected, probably due to the water present in tubing atmosphere, which comes from titania suspension and ammonia solution spray.

Intrinsic and specific activities of photocatalysts were calculated based on the surface area and mass of catalyst respectively, as shown in Table 2. Results indicate that the doping of nitrogen improves surface photocatalytic activity for all samples, and the highest values of intrinsic activity were obtained for sample N–TiO_2 800.

3.3. General discussion

Sample N–TiO_2 with thermal 600 °C was no affected in its surface area, nor in its anatase to rutile ratio, and according to the results of activity test, the doping of nitrogen was enough to enhance the photocatalytic activity, thus rate of phenol degradation is significantly higher for N–TiO_2 than the observed for TiO_2 photocatalyst without treatment.

The decrease in surface area of sample N–TiO_2 800 causes the loss of specific activity, but it has the most active surface. Since for this sample, the highest displacement of absorption radiation edge towards visible light is obtained, probably more nitrogen was inserted in the TiO_2 structure, and each square meter of photocatalyst was more active than the surface of the other samples, nevertheless, the sintering of particles reduced the available surface area to degrade phenol. Under the reaction conditions, the number of events per time unit to produce the hole–electron pair is increased as a consequence of the band gap reduction, but a lower formation of active species at surface per gram of photocatalysts is obtained. The formation of active species is limited by the available surface, and since for N–TiO_2 800 the number of excited states is higher, most of the photogenerated pairs recombine in the bulk mass.

Table 2
Specific and intrinsic activity of photocatalysts

Sample	Specific activity mmole transformed/g h	Intrinsic activity mmole transformed/m^2 h
TiO_2 P25	0.134	2.74
N–TiO_2 600	0.186	3.65
N–TiO_2 700	0.138	3.20
N–TiO_2 800	0.120	4.00

4. Conclusions

A thermal treatment under controlled atmosphere was developed to dope nitrogen atoms in titania Degussa P25 photocatalyst to increase its photocatalytic activity. Thermal treatment reduce significantly the surface area of samples at 800 °C, but the insertion of nitrogen narrowed the band gap, and under reaction conditions the result is an increase of photocatalytic activity of surface (i.e. each square meter of TiO_2 is more active).

The method was proved to modify the surface of TiO_2 nanoparticles by means of the insertion of nitrogen atoms, thus reducing the band gap. This modification increased the photocatalytic activity of TiO_2 under visible radiation; the narrowing of band gap was lower than 5%, but enough to increase the photocatalytic activity.

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