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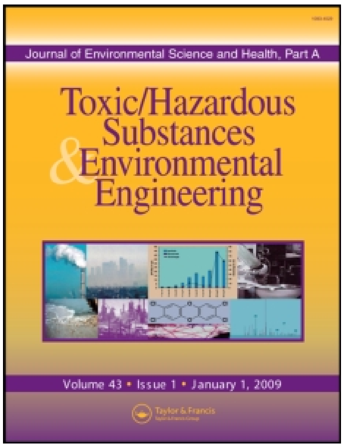

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Photodegradation of phenanthrene by N-doped TiO_2 photocatalyst

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The photodegradation of phenanthrene has been catalyzed by nanostructures of TiO_2 doped with nitrogen, N-doped TiO_2. The N-doped TiO_2 was prepared from the sol-gel reaction of Titanium(IV) bis(ethyl acetoacetato)diisopropoxide with 25% ammonia solution. The N-doped TiO_2 was calcined at various temperatures from 300 to 700°C. X-ray diffraction (XRD) results showed that N-doped TiO_2 remained amorphous at 300°C but anatase-to-rutile transformation started at 400°C and was complete at 700°C. The average particle size calculated from Scherrer's equation was in the range of 9–51 nm with surface area (S_{BET}) of 253.7–4.8 m^2/g. X-ray photoelectron spectroscopy (XPS) results confirmed the incorporation of nitrogen atoms (Ti-N bond) in the N-doped catalyst. Moreover, the percentage of nitrogen determined by Elemental analysis was 0.236% of N-doped calcined at 400°C. UV-Vis reflection spectra indicated that N-doped TiO_2 calcined at 400°C shifted to the higher absorption edge in the range of visible light. N-doped TiO_2 calcined at 400°C successfully catalyzed the photodegradation of phenanthrene (80% conversion) whereas N-doped TiO_2 calcined at 500°C and P25 TiO_2 failed as catalysts.

Keywords: N-doped TiO_2, photodegradation, phenanthrene, sol-gel.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) consisting of fused aromatic rings are very persistent in the environment and difficult to degrade biologically.[1] They originate from incomplete combustion or pyrolysis of organic matter such as petroleum, coal, tobacco and motor oil.[2] Most PAHs are released into rivers or atmosphere and accumulated in soils and sediments. Moreover, many are carcinogenic,[3–6] teratogenic[5] and/or mutagenic[6,7] and accordingly much recent research has focused on the studies of impacts of PAHs on health and potential routes for PAHs degradation.

One such possibility is photocatalytic degradation, in which photocatalysts are used in order to enhance degrading efficiency. TiO_2 is one of the most frequently used photocatalyst because of its availability, stability and low toxicity. Particularly, an anatase form of TiO_2 has previously been employed in many photodegradation reactions.[8,9] The photocatalytic mechanism involves irradiation of electron-hole pairs in the valence band of TiO_2 by light of energy higher than that of the band gap (3.2 eV for anatase phase).[10] Some electrons (e^-) are excited to the conduction band and holes (h^+) still remain in the valence band. Such holes act as a strong oxidizing agent reacting with water molecules or hydroxyl groups on the TiO_2 surface so as to generate hydroxyl radicals ($^{\cdot}OH$), which initiate photodegradation. Furthermore, the excited electrons can also react with oxygen molecules to form superoxide radicals ($O_2^{\cdot -}$), which subsequently react with protons (H^+) to produce hydroxyl radicals.[11]

TiO_2 was prepared using sol-gel route since it is an efficient method for tailoring nanostructured materials and is easy and simple to handle at room temperature.[12] The sol-gel preparation involves two reactions as follows,

1. Hydrolysis

$$\equiv \mathrm{Ti{-}O{-}R} + \mathrm{H{-}O{-}H} \rightarrow \equiv \mathrm{Ti{-}O{-}H} + \mathrm{R{-}O{-}H}$$

2. Condensation

$$\equiv \mathrm{Ti{-}O{-}X} + \mathrm{H{-}O{-}Ti} \equiv \rightarrow \equiv \mathrm{Ti{-}O{-}Ti} \equiv + \mathrm{X{-}O{-}H}$$

where X is an alkyl group or H.

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The rather high band gap energy (3.2 eV) of TiO_2 corresponds to the wavelength of UV light (<387 nm).[13] Since solar light consists mainly of visible wavelengths, there have been many attempts to decrease the TiO_2 band gap.[13–15] The present study substituted some of the TiO_2 oxygen atoms by nitrogen atoms. The resulting mixed states of N 2p and O 2p lower the band gap of TiO_2 so that irradiation of visible light can excite electrons from the valence band to the conduction band.[8,13]

The objectives of this work are to prepared and characterized N-doped TiO_2 nanoparticles. The as-prepared N-doped TiO_2 and P25 TiO_2 were used for the photocatalytic degradation of phenanthrene in visible region. Also, the photocatalytic efficiency of N-doped TiO_2 was compared with that of P25 TiO_2.

Experimental procedure

Catalyst preparation and characterization

Catalysts were prepared by addition of 5 mL of 25% ammonia solution to 10 mL of titanium(IV) bis(ethyl acetoacetato)diisopropoxide with stirring. The resulting mixture was incubated at 30°C for 1 h and then 120°C for 1 h to obtain pale yellow solid. Subsequently, the prepared solid was calcined at temperature between 300–700°C for 1 h to give catalysts for further characterization. The color of the prepared catalysts varied, depending on the calcination temperature, from brown at low temperature to white and light yellow at high temperature. Commercial TiO_2 (Degussa P25) was used as a reference catalyst.

Samples for X-ray powder diffraction (XRD) analysis was deposited on a silicon wafer sample holder and characterized using a Philips Pw 1830 X-ray diffractometer (Cu Kα, 1.5418 Å). X-ray photoelectron spectroscopy (XPS) was carried out at the Siam Photon Laboratory using a VG Scientific concentric hemispherical analyzer with an Al Kα (1486.68 eV) radiation source. UV-Vis reflection spectra from 250 to 800 nm were collected on a Perkin Elmer Lambda 650 spectrophotometer. Samples for transmission electron microscopy (TEM; JEOL 1200EX, 120 keV) were deposited on carbon-coated, 3 mm-diameter, electron microscope grids. Specific surface area, pore size distribution and pore volume of the prepared catalysts were calculated according to the Brunauer-Emmett-Teller (BET) method by using nitrogen adsorption-desorption data from the Autosorb-1 Quanta Chrome. Percentage of nitrogen in the photocatalyst was determined by LECO CHNS-932 Elemental Analyzer with using sulfamethazine as a standard material which consists of 51.78% C, 5.07% H, 20.13% N and 11.52% S.

Photocatalytic activity

Photocatalytic activity was determined by using the photodegradation reaction of phenanthrene under visible light. Degradation efficiency of phenanthrene was measured spectrophotometrically using a UV-Vis spectrometer (Perkin Elmer Lambda 35). Photodegradation of phenanthrene with/without catalysts under visible light was monitored by changes in absorption at 251 nm (A_{251}) associated with phenanthrene residue. Changes in A_{251} with time were converted to relative concentration of phenanthrene (C/C_0). Stock solution of 20 ppm phenanthrene in methanol/deionized water mixed solvent (1:3) was prepared freshly prior to undertaking the reaction. Typically, the reaction was carried out at 30°C in a 250 mL-flask, using a mixture consisting of 125 mL of 20 ppm phenanthrene and 0.1000 g of catalyst. The reaction mixture was stirred under visible-light-irradiation using a 190 W, Xe-lamp equipped with a HOYA UV 385 cut off filter. Samples were collected between 30 min to 8 h for determination of absorbance at 251 nm. In addition, products from the photodegradation of phenanthrene were analyzed using a gas chromatograph (GC; HP5890 series II; column HP-5MS, 30 m × 0.25 mm (i.d.); film thickness 0.25 μm) equipped with a mass spectrometer (HP 5989B).

Results and discussion

Characterization of catalyst

Figure 1 shows the X-ray diffractograms of N-doped TiO_2 calcined at different temperatures and P25 TiO_2. The N-doped TiO_2 provided an amorphous structure at 300°C.

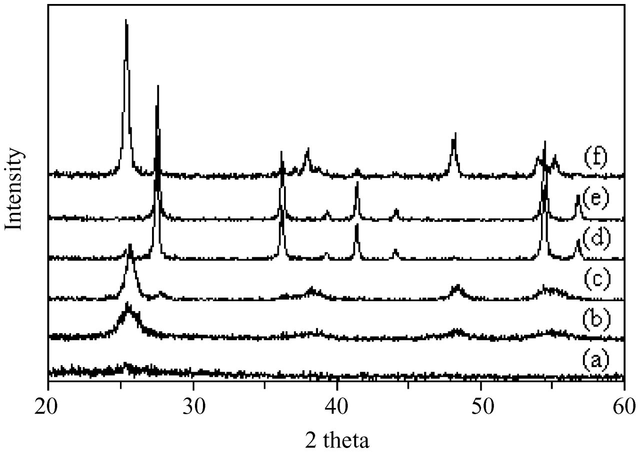

Fig. 1. XRD patterns of N-doped TiO_2 calcined at different temperatures (a) 300°C (b) 400°C (c) 500°C (d) 600°C (e) 700°C and (f) P25 TiO_2.

Table 1. The effect of calcination temperature on the crystallite size, the content of anatase phase, unit cell volume and surface area of N-doped TiO_2 and P-25 TiO_2; A for anatase and R for rutile.

Calcination temperature (°C)	*% Anatase*	*Crystallite size (nm)*	*Unit cell volume (Å³)*	*S_{BET} (m^2/g)*
400	78.125	8.84 (A)	132.03 (A)	253.7
500	81.576	13.13 (A) 21.53 (R)	135.72 (A)	74.0
600	7.443	50.81 (A) 28.18 (R)	61.85 (R)	4.8
700	1.569	35.53 (R)	61.82 (R)	—
P-25	74.834	22.61 (A) 40.86 (R)	131.31 (A) 61.61 (R)	49.2[a]

[a] See Cai, et al.[8]

The crystalline anatase phase at a 2θ of 25.40° corresponding to the (101) reflection started to appear at 400°C and increased in intensity with increasing calcination temperature. When the calcination temperature was increased to 500°C, the formation of rutile phase could be seen at a 2θ of 27.60° corresponding to the (110) reflection. Transformation of anatase to rutile phase was completed at 700°C. Furthermore, phase transformation also led to the decrease of unit cell volume from 135 Å^3 for anatase to 62 Å^3 for rutile. The average particle size was calculated applying Scherrer's equation[16] to the anatase (101) and rutile (110) diffraction peaks (the highest intensity peak for each pure phase). The average size of the catalyst particles is in the range of 9–51 nm as shown in Table 1.

Additionally, the surface area of N-doped TiO_2 was very drastically decreased from 253.7 m^2/g to 4.8 m^2/g with increasing temperature. The pore size distribution calculated from the desorption branch of nitrogen isotherm by the BJH method of the N-doped TiO_2 calcined at 400°C was in a range of 1.3–11.1 nm with an average pore diameter of about 2.9 nm, and pore volume of 0.1 cc/g. It was considered that the higher temperatures, the greater agglomeration. Nitrogen doping appeared to have no impact on the phase transformation and XRD pattern of TiO_2 since no other additional reflection was observed, except those of TiO_2. XRD pattern of P25 TiO_2 shows the presence of both anatase and rutile phases in different proportion.

In fact, the percentage of anatase phase was calculated in accord with the Spurr-Myers equation:

$$w_A = 1/(1 + (1.26)I_R/I_A)$$

where w_A is the weight fraction of anatase phase in the mixture and I_R and I_A are the intensities of the diffraction peaks of rutile and anatase phases, respectively.[17]

TEM micrograph of the N-doped TiO_2 calcined at 400°C shows the presence of nano-sized particles with spherical

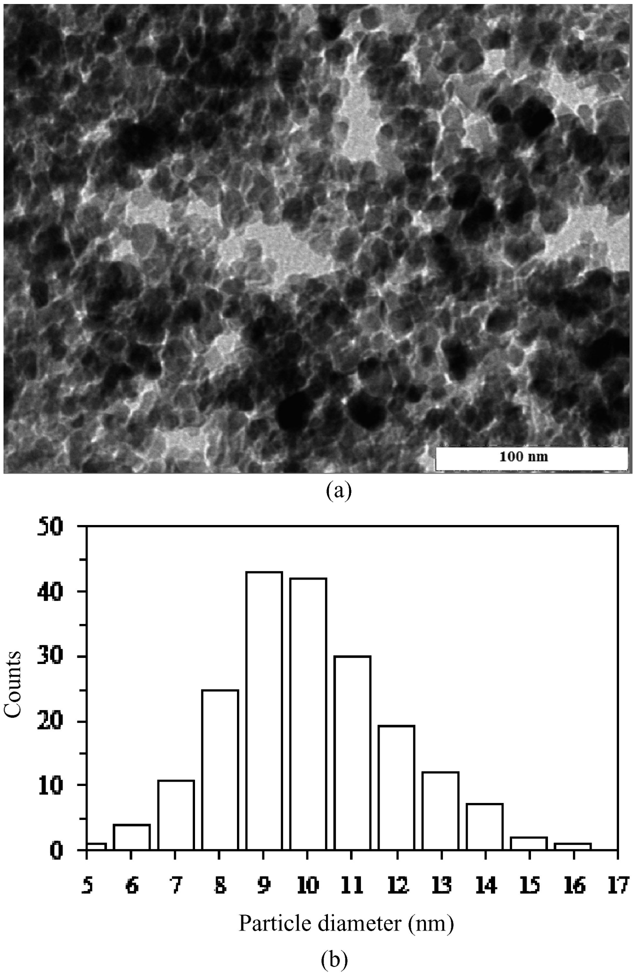

Fig. 2. (a) TEM micrographs of N-doped TiO_2 calcined at 400°C and (b) a histogram of the particle-size distribution.

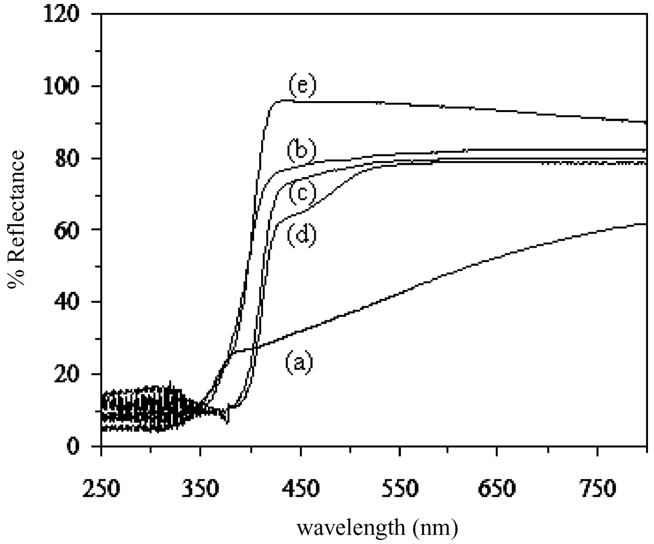

Fig. 3. UV-Vis reflection spectra of (a) N-doped TiO_2 calcined at 400°C (b) 500°C (c) 600°C (d) 700°C and (e) P25 TiO_2.

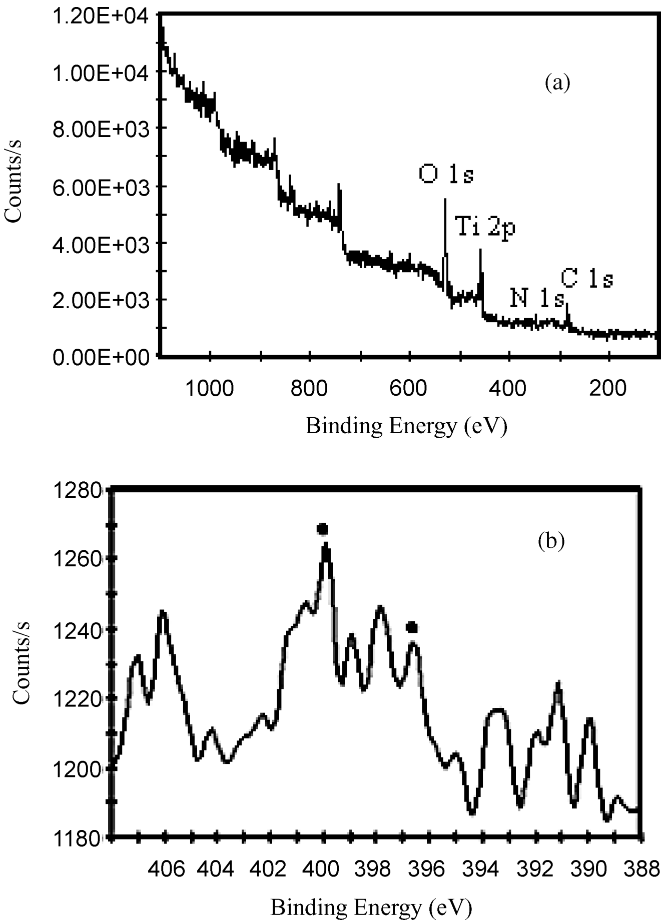

Fig. 4. (a) XPS spectrum of N-doped TiO_2 calcined at 400°C and (b) a magnified spectrum focusing on binding energy range of N 1s.

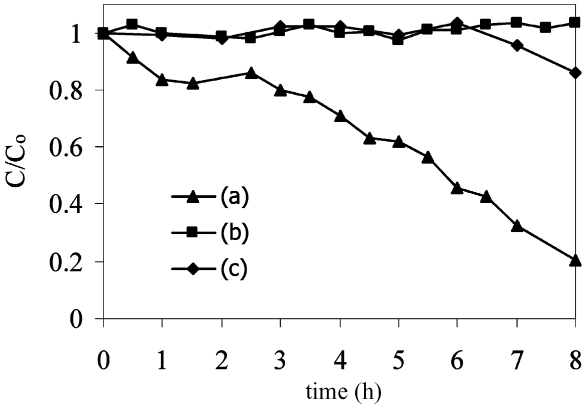

Fig. 5. Photocatalytic degradation of phenanthrene by (a) N-doped TiO_2 calcined at 400°C, (b) calcined at 500°C and (c) P25 TiO_2 (C/C_o is relative concentration).

morphology (Fig. 2). Histogram of the size distribution suggested that the N-doped TiO_2 particles were reasonably monodisperse with an average size of 10 nm, consistent with the value calculated from Sherrer's equation.

UV-Vis reflection spectrum of N-doped TiO_2 calcined at 400°C shows a low percentage of reflectance at wavelength longer 400 nm, indicating high absorption in visible region (Fig. 3, line a). It could be deduced that the 2p states of the substituted (doped) nitrogen atoms contributed to the band gap narrowing by mixing with O 2p states. Because of this narrower band gap an electron could be excited easily from the valence band to the conduction band in the doped metal oxide, thereby increasing the photocatalytic activity of the materials. With increasing calcination temperature, the spectra of the N-doped TiO_2 calcined at 500 and 600°C show less absorption in visible region while P25 TiO_2 nearly exhibits no visible absorption.

XPS spectrum of the N-doped TiO_2 calcined at 400°C (Fig. 4a) shows prominent photoelectron peaks for Ti 2p (458.5 eV), O 1s (530.3 eV) and C 1s (285.5 eV). Figure 4b exhibits the binding energy of N 1s at 397 eV, originating from Ti-N bonds in TiO_2 lattice,[8,18] whereas the peak at 400 eV was consistent with the chemisorbed N_2 molecules on the surface of TiO_2.[8] Moreover, the percentage of nitrogen found in N-doped TiO_2 calcined at 400°C by Elemental Analyzer was 0.236% higher than that of N-doped TiO_2 calcined at 500°C (0.036%).

Photocatalytic activity

The photocatalytic activity of the prepared catalysts was measured in terms of relative concentration of phenanthrene residue (Fig. 5). The results show that the N-doped TiO_2 calcined at 400°C efficiently catalyzed the decomposition of phenanthrene under visible light. It produced approximately 80% conversion of phenanthrene within 8 h. In contrast, using either N-doped TiO_2 calcined at 500°C or P25 TiO_2, only tiny proportions of phenanthrene degradation were observed (less than 10%). The high efficiency of the N-doped TiO_2 calcined at 400°C was presumably attributed to its smaller particle size and the greater number of active sites on its surface as well, of course, as its ability to absorb visible light.

Figure 6 shows the possible photodegradation pathway of phenanthrene based on the detection of bis(2-ethylhexyl)benzene-1,2-dicarboxylate at m/z of 390 and dimethyl-4-methyl-1,2-benzenedicarboxylate at m/z of 208 by GC/MS. This suggested that degradation of phenanthrene involved oxidation reaction by OH radicals, followed by ring opening of phenanthrene as previously reported.[19] Moreover, according to the US EPA, the LC_{50} of the two intermediate products for fish is 14 days, which is higher than that of phenanthrene.[20]

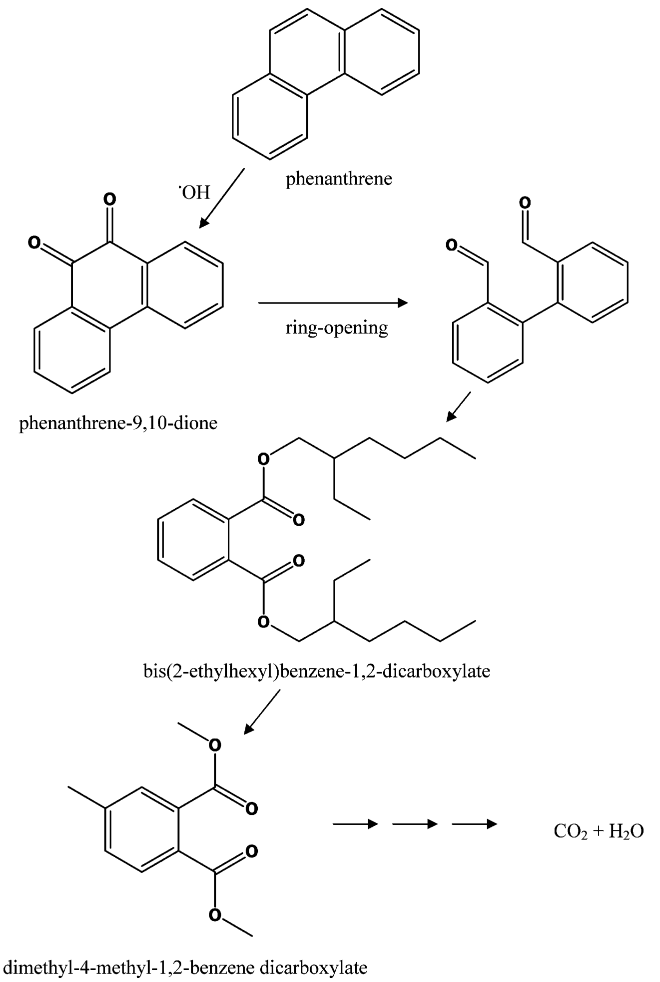

Fig. 6. The propose photodegradation pathway of phenathrene by using N-doped TiO_2 as a photocatalyst.

Conclusion

Nanoparticles of N-doped TiO_2 have been synthesized using a simple and effective sol-gel method involving a Ti-alkoxide precursor and ammonia solution. XRD diffractograms show that the N-doped TiO_2 undergoes the anatase-to-rutile phase transformation at calcination temperature range of 400–700°C and that N-doping has no impact on the TiO_2 lattice structure. However, N-doping is conducive to a concomitant narrowing of the band gap by generating N 2p states throughout the O 2p valence band, which is confirmed by the UV-Vis reflection spectra. Moreover, the XPS spectra indicate the TiO_2 structure to have some substitutional nitrogen atoms at a binding energy of 397 eV. The photocatalytic activity is measured by the photodegradation of phenanthrene. N-doped TiO_2 calcined at 400°C catalyzes this reaction under visible light. The catalytic pathway involves the generation of two intermediate products, bis(2-ethylhexyl)benzene-1,2-dicarboxylate and dimethyl-4-methyl-1,2-benzenedicarboxylate.

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