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Article

Solvothermal synthesis of N-doped TiO₂ nanoparticles using different nitrogen sources, and their photocatalytic activity for degradation of benzene

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ABSTRACT

Anatase-brookite mixed-phase N-doped TiO₂ (N-TiO₂) nanoparticles were synthesized through a solvothermal method using different nitrogen sources. The resulting samples were characterized by X-ray diffraction, specific surface area measurement, X-ray photoelectron spectroscopy, and standard and high-resolution transmission electron microscopy. The effects of the different nitrogen sources on phase composition, particle size, microstructure, and specific surface area are investigated. The photocatalytic activity of the TiO₂ samples was evaluated through photocatalytic degradation of gaseous benzene under UV-light irradiation. N-TiO₂ prepared using hydrazine hydrate achieved the highest photocatalytic performance in all the samples studied (including the commercial P25). Different intermediates during the photocatalytic degradation of benzene over HNT were identified by GC-MS analysis. A detailed reaction mechanism was proposed to explain their formation as intermediates in the reaction. Moreover, the photocatalytic activity of the nanoparticles remained almost unchanged after 15 gaseous-benzene degradation test cycles.

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1. Introduction

Volatile organic compounds (VOCs) are not only hazardous to human health but also harmful to the environment, and this important problem has stimulated the development of fundamental and applied research in the area of environmental remediation for these substances [1]. Benzene is one of the most hazardous VOCs and is listed as a priority pollutant because of its high toxicity, confirmed carcinogenicity, and environmental persistence [2,3]. Photocatalysis has received much attention in recent years because it is potentially a method for completely

decomposing toxic chemicals [4]. Among the photocatalysts studied over the past few decades, TiO₂ has attracted much research attention because of its high chemical stability, inexpensiveness, and nontoxicity [5–9]. However, TiO₂ photocatalysts used for treatment of gaseous benzene typically exhibit poor activity and stability because of the deposition of less reactive byproducts on the TiO₂ surface [10–12]. Researchers have applied a number of different strategies to overcome this major challenge and enhance the efficiency of photocatalytic oxidation. Doping TiO₂ with a noble metal (e.g., Rh, Pt, or Ag) improves the efficiency of benzene photocatalytic oxidation

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and boosts the durability of the TiO_2 catalyst [13–18]. However, transition metal ions can also act as electron-hole recombination sites, which could result in low photocatalytic efficiency [19,20]. Moreover, noble metals are usually very expensive, which is not conducive to industrial application. Therefore, finding a highly efficient and cost-effective strategy for removing benzene from the ambient environment remains a significant challenge.

N-doped photocatalysts have received much attention since Asahi et al. [21] reported on a visible-light-active N-doped TiO_2 photocatalyst. Researchers have developed various methods to prepare N-doped photocatalysts: sputtering [21,22], ion implantation [23,24], sol-gel [25–27], and chemical treatment of bare TiO_2 [28,29]. The photoactivity of N-doped TiO_2 (N- TiO_2) varies with the preparation method, the precursors used to dope the nitrogen, and the target pollutant. The solvothermal technique, which facilitates the control of grain size, particle morphology, microstructure, and phase composition, has garnered more and more attention for preparing TiO_2 nanoparticles. Recently, Jing et al. [30] prepared a TiO_2 photocatalyst through a hydrothermal method and found that its activity for dimethyl phthalate (DMP) degradation was 2.5 times more than that of TiO_2 produced by a sol-gel process. Jacoby et al. [31] reported the formation of phenol, malonic acid, hydroquinone, benzoic acid, and benzoquinone on the surface of TiO_2 in the case of benzene oxidation. Analysis of the products recovered from used TiO_2 can provide information about the degradation mechanisms.

In this work, we focus on the preparation method and the precursors used for nitrogen doping because they have a noticeable effect on the photoactivity of N- TiO_2 . We prepared three types of N- TiO_2 by the solvothermal method and characterized the various N- TiO_2 samples by means of X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET) surface area measurements, X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and high-resolution transmission electron microscopy (HRTEM). We also investigated the effects of the nitrogen source on phase composition, particle size, microstructure, specific surface area, and photocatalytic activity. Finally, we evaluated the photocatalytic activity of the prepared N- TiO_2 powders in the photocatalytic degradation of gaseous benzene under UV irradiation in air. The reaction products that adhered to the used TiO_2 sample were identified by gas chromatography-mass spectrometry (GC-MS). On the basis of these analyses, degradation mechanism was suggested.

2. Experimental

2.1. Preparation of the catalyst

In a typical synthesis, tetrabutyl titanate (TBOT, 5 mL) was added to anhydrous isopropanol (20 mL) to obtain solution A. In a separate 250 mL round-bottom flask, deionized water (10 mL) and glacial acetic acid (1 mL) were added to anhydrous isopropanol (10 mL). Next, a nitrogen source (ammonia, hydrazine hydrate, or ammonium nitrate) was added to the flask to obtain solution B (N/Ti = 1). Solution A was added drop-wise

to solution B, and the mixture was then stirred for 1 h. The resultant mixture was then transferred into a 100 mL stainless steel autoclave with a Teflon inner liner, which was kept at 453 K for 5 h to allow complete TBOT hydrolysis and crystallization. After the solvothermal treatment, the powdered product was separated by centrifuging, washed with distilled water and absolute ethanol twice, and then dried at 333 K for 18 h. The dried compound was then calcined at 623 K in air for 1 h to obtain nanoparticles of N- TiO_2 . The sample prepared in the presence of ammonia was denoted as ANT, that prepared with hydrazine hydrate as HNT, and with ammonium nitrate as NNT. Another TiO_2 sample was prepared in a similar process but in the absence of a nitrogen source as a control, and was denoted as PT.

2.2. Characterization

XRD patterns of all samples were recorded on a PANalytical X'Pert PRO X-ray diffractometer with $\text{Cu K}\alpha$ radiation. TEM and HRTEM analyses were taken with a Tecnai G20 TEM using an accelerating voltage of 200 kV. The BET surface area and porous structure of the samples were evaluated on the basis of nitrogen adsorption isotherms measured on a Quantachrome Autosorb-1-C-MS. XPS measurements were carried out with a VG Multilab 2000 (Thermo Scientific) spectrometer using $\text{Al K}\alpha$ ($h\nu = 1486.6$ eV) radiation. XPS data were calibrated with respect to the binding energy of C 1s at 284.6 eV. The elemental analysis was carried out on a vario Micro cube (Elementar, Germany). Adsorbed intermediates were extracted from the used TiO_2 samples with chloroform and then condensed using a rotary evaporator. The photooxidation intermediate products were then identified using an Agilent 7890A/5975C GC-MS equipped with a DB-WAX capillary column.

2.3. Photocatalytic activity

The photocatalytic activity of TiO_2 samples for the decomposition of gaseous benzene in the air under UV irradiation was measured using a 6.5 L stainless steel gas-phase batch reactor with a quartz window. The reactor was connected, through an automatically sampling 10-way valve (VALCO) with an air actuator, to a gas chromatograph (GC-9560, Huaai Inc., Shanghai, China) equipped with a methane converter, a Porapak R column and PEG20M column, and a flame ionization detector (FID). A thermocouple was put onto the TiO_2 powder to measure its temperature. Heaters were used to hold the reaction temperature of the photocatalytic system at about 363 K to ensure complete benzene evaporation. A UV lamp (250 W, 365 nm, Hg) was used as a light source to trigger the photocatalytic reaction. The catalysts (0.5 g of catalyst powder) were prepared by coating an aqueous suspension of the TiO_2 powder to be tested onto a 12-cm-diameter glass dish, which was set on the bottom of the reactor. The lamp was turned on until the measured concentration of CO_2 remained unchanged to ensure the removal of all adventitious organic compounds adsorbed on the TiO_2 catalyst and establish adsorption-desorption equilibrium of CO_2 on the TiO_2 catalyst. The lamp was then turned

off, and 2 μL benzene was injected into the reactor to give a concentration of benzene of about 180 mg/m^3 in the reactor. Prior to photocatalytic oxidation, benzene vapor diluted with air was pre-adsorbed on the catalyst without illumination. Subsequently, the oxidation was commenced with the UV lamp turned on. The concentration of CO_2 produced was obtained by subtracting the initial concentration of CO_2 in the reactor. All the comparison experiments were conducted under the same conditions. The procedure for the experiments that recycled the TiO_2 catalyst was as follows. After the first catalytic activity test, the reactor was opened to remove the products (e.g., CO_2) and allow fresh air to enter, and then covered again. Then, benzene (2 μL) was injected into the reactor, and the lamp was turned on to start the next test of catalytic oxidation. Twenty cycles were carried out.

3. Results and discussion

3.1. XRD results

XRD was used to investigate the crystallite size and phase structure of the photocatalysts. Figure 1 shows the XRD patterns of pure TiO_2 and the N- TiO_2 nanoparticles prepared from different nitrogen sources. All of the TiO_2 samples consist of anatase with a small amount of brookite. Earlier investigators have also reported overlap of the peaks from the anatase and brookite phases, suggesting the need for a numeric deconvolution technique to separate these peaks [32]. However, because clearly distinguished higher angle peaks of anatase (204) and brookite (121) are easy to identify in Fig. 1, we have not tried to develop a numerical deconvolution approach. Instead, we es-

Fig. 1. XRD patterns of pure TiO_2 and N- TiO_2 nanoparticles prepared by solvothermal treatment with different nitrogen sources.

Table 1

Structural properties of the photocatalyst samples.

Sample	Main phase composition	Crystallite size (nm)	Content of B (%)	Average pore size (nm)	Pore volume (cm^3/g)	$S_{\text{BET}}/(\text{m}^2/\text{g})$
PT	Anatase+Brookite	7.6	6.4	10.2	0.39	153.0
HNT	Anatase+Brookite	7.5	9.6	10.9	0.41	149.9
ANT	Anatase+Brookite	9.9	19.9	13.1	0.39	120.6
NNT	Anatase+Brookite	7.0	12.3	9.4	0.41	173.3

Fig. 2. N_2 adsorption-desorption isotherms (a) and the corresponding pore size profiles (b) of pure TiO_2 and N- TiO_2 nanoparticles.

timate the brookite phase content of the mixture from the XRD peak intensity [33]. The results of this analysis, summarized in Table 1, suggest that ammonia and ammonium nitrate promote more brookite formation, and that less brookite forms when hydrazine hydrate is used.

We also found that the crystallite size and the type of nitrogen source are strongly related. The diffraction peaks of NNT are broadened, indicating the formation of smaller TiO_2 crystallites. However, the diffraction peaks are lower for ANT, indicating a decrease in the degree of crystallinity. The average crystallite size of all these samples are summarized in Table 1.

3.2. N_2 adsorption results

Figure 2(a) shows the N_2 adsorption-desorption isotherms of the N- TiO_2 samples; the isotherms belong to type IV with an H3 type hysteresis loop [34]. The hysteresis loops occur at high relative pressures and are associated with the capillary condensation of gases within the mesopores. Figure 2(b) shows the corresponding pore size distribution curves. The monomodal pore size distribution in the mesoporous region is mainly asso-

ciated with primary intra-aggregation of nanocrystals of uniform size. The surface areas (S_{BET}), pore volumes (V_{p}), and average pore size (APS) of the different samples, calculated from the N_2 adsorption-desorption isotherms using the BJH method, are summarized in Table 1. All samples show higher specific surface areas in the range of 120.6–173.3 m^2/g , much larger than the surface area of commercial P25 (44 m^2/g) [35]. Moreover, the S_{BET} values depend strongly on the nitrogen source. The surface area of ANT (120.6 m^2/g) is significantly less than that of pure TiO_2 (153.0 m^2/g), indicating that using ammonia in the preparation may result in aggregation of particles.

3.3. XPS and elemental analysis

We next used XPS to investigate the chemical compositions and elemental states of the as-prepared samples. Figure 3 shows the existence of N, C, O, and Ti in these powders. The Ti 2p region is near 460 eV, the O 1s region is near 530 eV, and the N 1s region is near 400 eV. The Ti 2p binding energy peaks for HNT and NNT appear at 458.47 and 458.46 eV, respectively, lower than the peak seen for P25 powder (459.7 eV). The O 1s peaks of HNT and NNT appear at 529.67 and 529.66 eV, respectively, and are also lower in energy than the corresponding P25 peak (530.8 eV). This indicates that the O or Ti atoms in the doped samples are substituted by other atoms. This substitution is confirmed by the (101) surface peaks of the HNT and NNT samples, which shift slightly to higher values of 2θ compared with PT in the XRD results. The binding energy peaks for HNT and NNT extend from 397 to 404 eV. In particular, there is an XPS peak at about 400 eV (N 1s) for the HNT and NNT sam-

ples.

Identification of the nitrogen species in N- TiO_2 samples has also been a subject of controversy. Note that Figure 3 shows no N 1s XPS peaks with binding energy of 396–397 eV for the Ti-N compounds, which means that the doped-N can be in an interstitial position, directly bound to the lattice oxygen, but cannot occupy the lattice oxygen sites. Therefore, we have assigned the N 1s XPS peak of the N- TiO_2 samples at 400 eV to a Ti–O–N bond [36]. The N/Ti atomic ratios for HNT and NNT estimated from the XPS spectra are 1.48% and 1.62%, respectively. Moreover, according to elemental analysis, the nitrogen contents were about 0.80%, 0.91%, and 0.57% for HNT, ANT, and NNT, respectively.

3.4. TEM and HRTEM

The N- TiO_2 powders were also investigated by TEM, and images are shown in Figure 4. The average crystal size is larger in the presence of ammonia (ANT) than for pure TiO_2 , and the size distribution is broader. As shown in Table 1, the crystallite size of ANT (9.9 nm) is significantly larger than that of PT (7.6 nm), indicating that ammonia negatively affects grain growth. However, the HNT and NNT samples have smaller crystal size than PT. Figure 4 also shows that the primary particles of HNT are relatively uniform, and that their size is in agreement with the value determined by XRD analysis. This indicates that hydrazine hydrate gives rise to better-dispersed TiO_2 particles than those prepared using ammonia and ammonium nitrate.

HRTEM images of the N- TiO_2 powders are given in Figure 5. The N-doped nanocrystals are highly crystalline, exhibiting well-resolved lattice structure. The observed spacing between the lattice planes of the samples is around 0.360 nm, which is in agreement with the distance between the (101) crystal planes of anatase TiO_2 . The images of the HNT, ANT, and NNT samples show lattice fringes with spacing around 0.250 nm, corresponding to the crystallographic planes of brookite TiO_2 (012);

Fig. 3. XPS survey spectra (a) and enlarged picture of N 1s high-resolution XPS spectra (b) of HNT and NNT.

Fig. 4. TEM images of HNT (a), ANT (b), NNT (c), and PT (d).

Fig. 5. HRTEM images of HNT (a), ANT (b), NNT (c), and PT (d).

these fringes are not seen in the image of the PT sample. The HRTEM results are consistent with the XRD results discussed above.

3.5. Photocatalytic ability

The photocatalytic activity of the TiO₂ samples was tested for the photodegradation of gaseous benzene in air. Figure 6 shows the conversion of benzene under UV irradiation. The HNT sample shows the highest performance in this photocatalytic process. The photocatalytic conversion ratio of benzene over HNT is 95.9% after 150 min, and Fig. 7 shows that the amount of CO₂ produced over HNT is up to 375.84 mg/m³, which is much higher than that produced over P25 (192.01 mg/m³). In contrast to the HNT catalyst, the conversions of benzene over NNT, ANT, PT, and commercial P25 are 91%, 72.7%, 84.6%, and 67%, respectively. The data in Fig. 8 show that the photocatalytic conversion of benzene generally follows first-order kinetics, and the rate constant for HNT ($k = 18.7 \times 10^{-3} \text{ min}^{-1}$) is higher than those for PT ($k = 11.9 \times 10^{-3}$

Fig. 6. Benzene conversion over N-TiO₂ samples and pure TiO₂ nanoparticles under UV light.

Fig. 7. CO₂ concentration vs reaction time during the photocatalytic degradation of benzene.

min⁻¹) and P25 ($k = 7.3 \times 10^{-3} \text{ min}^{-1}$). We also found that ANT shows lower photocatalytic performance; this is consistent with its lower anatase content, smaller BET surface area, and broader particle size distribution. Thus, ammonia had a negative effect on the solvothermal synthesis of N-TiO₂ nanoparticles.

3.6. Photocatalysis mechanism

To investigate the mechanism of photodegradation and destruction of benzene, adsorbed intermediates were extracted from the used HNT sample by ultrasonication in chloroform. The resulting solution was evaporated to concentrate any dissolved intermediates, and the concentrated solution was analyzed by GC-MS for intermediates. Figure 9 shows the intermediates from HNT detected by GC-MS. The detected compounds included propanol, 3-buten-2-ol, 2,3-epoxyhexane, 1,2,3-trimethylcyclohexane, and 3-methylcyclopentanol. Zhong et al. [37] noted that alkyl radicals such as CH₃•, CH₃CH₂•, and CH₃CH₂CH₂• could be formed during benzene photocatalytic oxidation. Kislov's results [38] showed that when a benzene molecule absorbs a sufficiently energetic photon, it can split apart into CH₃•, C₂H₃•, C₆H₅•, and other products after further isomerization and splitting. On the basis of the identified in-

Fig. 8. $\ln(C_0/C)$ vs reaction time for photodegradation of benzene.

Fig. 9. Mass spectra of the intermediates for the photocatalytic degradation of benzene.

intermediates, possible photocatalytic degradation pathways for benzene are proposed in Scheme 1. Under our experimental conditions, hydroxyl radicals ($\text{OH}\cdot$) have been regarded as a key species in the photocatalytic degradation of benzene; in the presence of O_2 , these radicals can react with benzene to form various alkyl radicals, such as $\text{CH}_3\cdot$, $\text{CH}_3\text{CH}_2\cdot$, and so on. After a series of free radical reactions, the benzene molecules were degraded into ring-opened products and some shorter aliphatics; finally, they were mineralized to CO_2 and H_2O .

3.7. Photocatalyst stability

To test the stability of the N-TiO₂ samples under UV irradiation and evaluate the photostability and reusability of HNT, we conducted a series of experiments to observe the photodegradation of gaseous benzene under UV irradiation. As shown in Fig. 10, the photocatalytic activity of HNT remains almost unchanged after 15 use cycles, indicating that HNT exhibits excellent photostability. Recent theoretical calculations showed that N-doping led to a substantial reduction of the energy cost to form oxygen vacancies in the bulk TiO₂ [39]. Many studies had confirmed that the formation of the superoxide radicals required oxygen vacancy sites, which could then generate active

Scheme 1. Photocatalytic oxidation mechanism of benzene.

Fig. 10. The photostability of HNT under UV irradiation for the photocatalytic oxidation of benzene.

OH• radicals [40]. Moreover, the doped nitrogen is able to avoid recombination of photogenerated e^-h^+ by preventing electrons from jumping back to the valence band, causing the photoinduced electrons to be captured by the oxygen adsorbed on the surface of the catalyst [41]. This process makes it feasible for photogenerated electrons to transfer to the catalyst surface and facilitates the photooxidation of gaseous benzene.

4. Conclusions

Three types of N-TiO₂ were prepared from different nitrogen sources by a solvothermal method. Hydrazine hydrate had the most beneficial effects on the chemical structure of the obtained N-TiO₂ nanoparticles, and the N-TiO₂ catalyst made using hydrazine hydrate (HNT) achieved the highest photocatalytic performance in the degradation of gaseous benzene. Moreover, the photocatalytic activity of HNT remained virtually unchanged after being recycled 15 times. Thus, the high photocatalytic activity and good photostability of N-TiO₂ prepared using hydrazine hydrate as a nitrogen source should facilitate its application in degradation of gaseous benzene. Different intermediates have been identified during the photocatalytic degradation of benzene by GC-MS analysis. A detailed reaction mechanism is proposed to explain their formation as intermediates in the reaction.

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Graphical Abstract

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Solvothermal synthesis of N-doped TiO₂ nanoparticles using different nitrogen sources, and their photocatalytic activity for degradation of benzene

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Anatase-brookite mixed-phase N-doped TiO₂ (N-TiO₂) nanoparticles were synthesized. N-TiO₂ prepared with hydrazine hydrate achieved the highest photocatalytic performance and could be reused at least 15 times in the degradation of gaseous benzene.

不同氮源溶剂热合成N-TiO₂纳米颗粒及其光催化降解气相苯

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摘要: 采用三种不同的氮源溶剂热合成了锐钛矿-板钛矿混晶的N-TiO₂催化剂. 采用X射线衍射、N₂吸附-脱附、X射线光电子能谱和透射电子显微镜等手段对催化剂进行了表征. 重点研究了不同氮源对催化剂的相组成、晶粒尺寸、微观结构以及比表面积的影响. 采用紫外光降解气相苯测试了合成材料的催化活性. 结果表明, 以水合肼为氮源合成的N-TiO₂表现出最优的光催化活性, 其活性明显高于P25, 且能够循环使用15次以上. 采用气相色谱-质谱技术分析了光降解过程的中间产物, 基于此提出了相应的降解机理.

关键词: 氮掺杂二氧化钛; 溶剂热合成; 光催化降解; 气相苯; 光催化机理

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