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Effect of Ammonia Thermal Treatment on the Structure and Activity of Titanium Oxide Photocatalysts

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Different titanium oxide powders (ATiO₂, BTiO₂) were pretreated in ammonia (NH₃) gas at high temperatures. After the pretreatment, the color of the titanium oxide powders changed from white to yellow or gray depending on the pretreatment temperatures. Morphologies and structures of the treated titanium oxide powders were characterized by physical chemical methods. XRD measurements showed that the crystalline structures were mainly mixture of anatase and rutile for the ATiO₂ but only anatase for the BTiO₂. Stronger absorption of visible light was observed for both types of samples using UV-Vis diffuse reflectance spectra. X-ray photoelectron spectroscopy demonstrated that doped nitrogen existed on the surface TiO₂ after ammonia gas pretreatment. The photocatalytic activities of the treated titanium oxide samples were evaluated via the photodegradation of methyl orange and phenol in aqueous suspensions. No obvious improvement in photocatalytic activity was achieved by ammonia pretreatment although it could enhance the absorption of light. Effects of treatment temperatures on photoactivities were complete different for ATiO₂ and BTiO₂ (i.e. higher treated temperatures yielded higher activities for BTiO₂ but lower for ATiO₂). All samples yielded lower activity levels after ammonia pretreatment without regard to pretreatment temperature or the reaction light resource.

Key words: Titanium oxide, Ammonia, Photocatalysis, Nitrogen, Oxygen vacancies

I. INTRODUCTION

Much of the use of semiconductors as photocatalysts, in the past two decades, has been driven by their potential application in photooxidation reactions for eliminating toxic organics from aqueous or gaseous phase environments [1-4]. Photocatalysis by titanium dioxide (TiO₂) has been demonstrated to be an effective method for removing pollutants in water and air. Apart from being indiscriminate and capable of degrading many different types of organic pollutants, the TiO₂ catalysts employed are relatively stable, nontoxic, commercially available and inexpensive [5-7]. However, due to its band-gap energy (3.20 eV for anatase and 3.03 eV for rutile), pure TiO₂ can only be activated by short-wavelength UV light with wavelength below 387 nm. A very small fraction (about 3%-5%) of the solar spectrum satisfies this energy level. As a result, it is necessary to dope or modify the TiO₂ to extend its light absorption into the visible region.

Visible light photoactivity has been brought about in TiO₂ by doping it with nitrogen [8,9], carbon [10,11], dyes [12,13], or with transition metals [14-16]. Thermal treatment by some reductive gases is a potential substitution method for modifying titanium oxide in or-

der to induce higher activity or to expand absorption of visible light. Okamoto adopted H₂ reduction as a simple pretreatment of TiO₂ in photocatalytic degradation of phenol [17]. Heller reported the enhanced photocatalytic activity of the TiO₂ catalyst by a thermal reduction treatment using hydrogen gas at 550 °C [18]. Liu reported using the H₂-treatment of TiO₂ catalysts significantly enhanced the photodegradation rate of SSA and phenol [19]. Asahi found higher visible photocatalytic activity of the anatase TiO₂ treated in the NH₃(67%)/Ar atmosphere compared to the untreated one [8]. After thermal treatment under reductive gas, such as hydrogen or ammonia, oxygen vacancies (OV) and trivalent titanium (Ti³⁺) may be present in the modified TiO₂. This may account for the higher photocatalytic activities as the reduction of TiO₂ particles raised their Fermi level and increased the height of the barrier that repels electrons from the particle's surface. This is because of more Ti³⁺ available in the TiO₂ particles. Furthermore, thermal treatment by ammonia not only results in the oxygen vacancies and trivalent titanium but also dopes nitrogen in the TiO₂ crystal lattice. Just as nitrogen doped TiO₂ can show higher activity and visible light absorbance (activity), so too, composite effects of doping nitrogen, oxygen vacancies and trivalent titanium by ammonia thermal treatment on TiO₂ photocatalysts may show significant results.

In this work, we prepared nitrogen-doped TiO₂ by hydrolyzing titanium sulfate in an ammonia solution. Next, an ammonia gas thermal treatment was used on

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the TiO₂. A chemical TiO₂ was also used for comparison. The correlation between the photocatalytic activity and the change of TiO₂ structure by ammonia thermal treatment was studied, in which methyl orange and phenol were tested as model pollutants.

II. EXPERIMENTAL SECTION

A. Materials

Titanium sulfate (CP) was purchased from Shanghai Qianjin Chemical Company, Shanghai. The Ammonia solution was purchased from Shanghai Suyi Chemical Reagent Company. Methyl orange and phenol were purchased from Shantou Xilong Chemical Factory and Nanjing Chemical Reagent No.1 Factory respectively and used without further purification. All other chemical reagents were of analytical grade.

B. Catalyst preparation

A chemical reagent, titanium oxide, was purchased and calcined at different temperatures (400, 500, 600, and 700 °C) for 2 h at 3 °C/min heating rate, in ammonia/argon (120 mL/min, 67% ammonia and 33% argon) at which point their color changed to either yellow or gray. The sample is denoted as ATiO₂. The powder calcined in air is denoted as aTiO₂.

An ammonia solution (at 30% concentration) was titrated into the titanium sulfate (concentration 20%) at 1 mL/min while stirred, until the pH reached 9. Temperature of the solution was maintained at about 20 °C. White sediment formed while the ammonia solution was introduced, the sediment was then rinsed in deionized water for 60 min and dried at 85 °C for 12 h. A white powder formed after the sediment dried. It was then ground in an agate mortar until the particles were smooth. The powder was calcined at different temperatures, as the former samples had been, and the color likewise changed to yellow or gray. The sample is denoted as BTiO₂ and the one calcined in air as bTiO₂.

C. Catalyst characterization

X-ray diffraction (XRD) patterns were obtained using a diffractometer with Ni filter and graphite monochromator (model D/max-rA from Rigaku, JAPAN). The X-ray source was Cu K α radiation ($\lambda=1.54187$ Å), and the 2θ ranged from 20° to 80°. The crystal size was determined from diffraction peak broadening by the Scherrer equation. High-purity silicon powder was used as calibration standard to account for any instrumental line broadening effect during crystal size estimation. UV-Vis diffuse reflection spectra (DRS) were recorded by a Shimadzu UV-240 spectrometer with a scan range

of 200 to 800 nm with a diameter of 150 mm integral ball. Standard magnesium oxide was used as the reference. X-ray photoelectron spectroscopy data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W Al K α radiation. The base pressure was about 0.3 μ Pa. The binding energies were referenced to the C1s line at 284.6 eV from adventitious carbon.

D. Photocatalytic activity measurement

To evaluate the photocatalytic activities of the TiO₂ powders, the photoreactivity experiments were carried out in a reactor containing 50 mg of catalyst and 100 mL of methyl orange, corresponding to a concentration of 10 mg/L. Prior to irradiation, the suspensions were stirred in the dark for 10 min to ensure adsorption/desorption equilibrium. After equilibrium, an ultraviolet light lamp with 254 nm wavelength was used on the photoreactor. At given irradiation time intervals, 4 mL aliquots were sampled, centrifuged, and subsequently filtered through a Millipore filter (pore size 0.45 μ m) to remove TiO₂ particles. The filtrates were analyzed by recording the adsorption band maximum in the UV-Vis spectra of the substances using a 751 UV-VIS (Shanghai) spectrophotometer.

In order to compare the photocatalytic activities for different light sources, further experiments were conducted under sunlight. The reactor contained 50 mg of catalyst and 100 mL of aqueous solutions of phenol corresponding to a concentration of 10 mg/L, the mixture was agitated for 10 min in the dark in order to reach adsorption and desorption equilibrium. Then sunlight was used. A filter glass was used to cut the light of wavelengths shorter than 420 nm and as only visible light can be used in phenol photocatalytic reaction. Samples were analyzed, identically to the aforementioned ones, for UV reaction with methyl orange except where the adsorption band maximum was different from phenol.

Characterization of degradation products is beyond the scope of this study. All tests were done in a consistent fashion, in order to achieve comparable results.

III. RESULTS AND DISCUSSION

A. XRD analysis

The XRD patterns are shown in Fig.1. The crystal size was determined from the diffraction peak broadening by the Scherrer equations, and the size of the anatase crystallites demonstrates the titania as the nanocatalysts. The BTiO₂ exhibited only anatase structure, where ATiO₂ yielded a combination of anatase and rutile. Higher crystallization was found for BTiO₂ pretreated at higher temperatures where the shape of the peaks were sharper, but there was no ob-

viously different crystallization for ATiO_2 pretreated at different temperatures. We have reported the XRD patterns of the given samples calcined in air before [20], these were almost the same for the TiO_2 calcined in air or in ammonia. Therefore, it could be concluded that the process of crystallization was not affected by the ammonia treatment. The crystal size of the BTiO_2 was much smaller than ATiO_2 , although high particle aggregation occurred in BTiO_2 as the phenomenon was often observed for the samples prepared by hydrolysis [20].

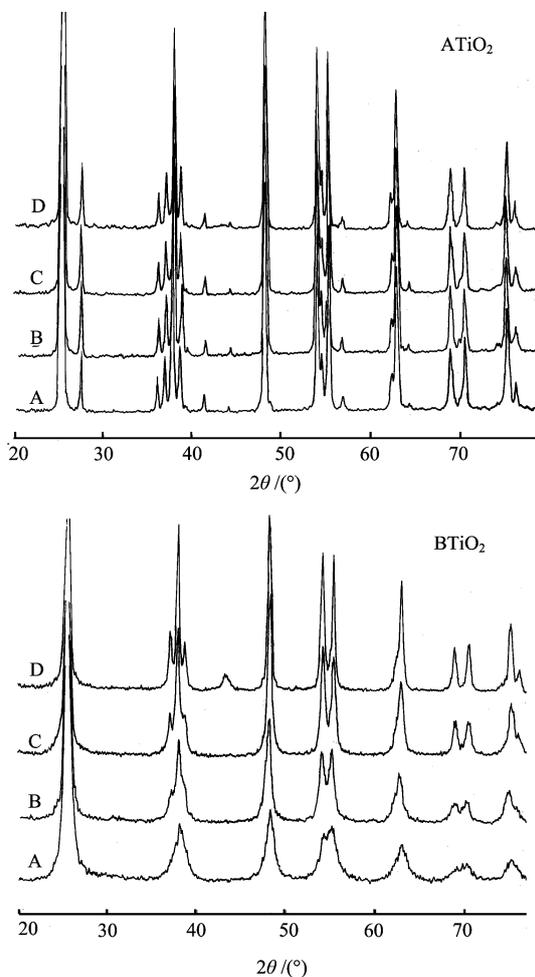


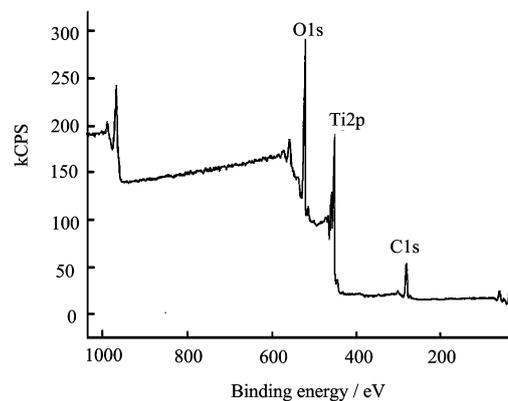
FIG. 1 XRD spectra of the ATiO_2 and BTiO_2 . A. 400 °C, B. 500 °C, C. 600 °C, D. 700 °C.

In the XRD patterns of all photocatalysts only the peaks for TiO_2 appeared, peaks of nitrogen and nitrogen-related compounds were undetected. This indicates that the nitrogen was loaded in an ionic state or as small as non-detectable particles. This was in contrast to metal doped TiO_2 in which the doping of metal substituted the Ti^{4+} . However, for nitrogen doped TiO_2 , the O atom was replaced by nitrogen. Asahi prepared nitrogen doped TiO_2 and found the N/Ti ratio was 0.0075 and the O/Ti ratio was 1.9925 [8], this indi-

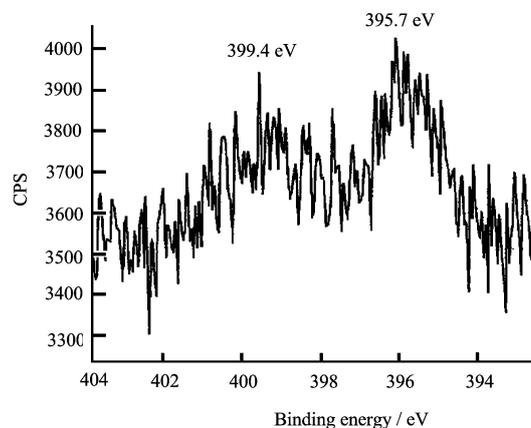
cated the O atom in TiO_2 was substituted by nitrogen atom. From XPS results they proposed that nitrogen doping was responsible for the visible activity of TiO_2 .

B. XPS measurement

Figure 2 shows the X-ray photoelectron spectroscopy data of the BTiO_2 calcined at 700 °C. In addition to titanium and oxygen, weak signals of nitrogen were measured at 395.7 and 399.4 eV. This gave the definite proof that ammonia pretreatment resulted in the formation of nitrogen doped titania. Saha investigated the N1s XPS spectra during the oxidation process of TiN and assigned the peaks as atomic $\beta\text{-N}$ (396 eV) and molecularly chemisorbed $\gamma\text{-N}_2$ (400 and 402 eV) [21]. Therefore the observed 395.7 and 399.4 eV peaks could be attributed to the atomic and molecular nitrogen on the surface TiO_2 . Lower binding energy in the nitrogen may indicate the chemical environments of the element were not the same as that of TiN and molecular N_2 . This



(A) XPS spectrum of titania distribution



(B) Expansive XPS spectrum of nitrogen 1s

FIG. 2 X-ray photoelectron spectroscopy of the ammonia gas thermal treated BTiO_2 at 700 °C for 2 h.

meant the N formed a doping structure but not as the formation of TiN or freely or adsorbed N₂. The result was confirmed as the XRD also showed that nitrogen-related compounds had not been formed. Also the different electron binding energies of atomic and molecular chemisorbed nitrogen indicated the N was not a simplex formation in the TiO₂, but it could produce different valence levels in the TiO₂. Some studies have argued for the influence of different valences of metal on the activity of photocatalyst [22], and which may play important roles in affecting charge trapping, release and migration, recombination, and interfacial charge transfer, and thus the photocatalytic behavior. Since the electron binding energy was alterable, the doped N's effect on the photochemical behavior was expected. Considerable carbon was observed in the sample, this may indicate that TiO₂ can selectively adsorb hydrocarbon or other carbon compounds. The atomic number ratio of N/Ti was about 5.18% and Ti/O was about 41.2%. As the concentration of unrecognized carbon on the surface was too high, no useful information about doping structures, such as TiO_{2-x}N_x, was reported by Asahi [8].

C. UV-Vis diffuse reflectance spectra

The UV-Vis diffuse reflectance spectra (DRS) of TiO₂, thermally treated with ammonia gas and calcined at different temperatures, showed no absorption variance in the UV range. The results are shown in Fig.3. In the visible range, a stronger absorption could be observed for each sample. From the optical point of view, this means that the samples were yellow or gray. Titania had light absorbance characterized under 387 nm, absorption in the visible range means photoelectric chemical character of the titania was changed by the ammonia gas treatment. This gave another information that ammonia treated titania was doped with nitrogen but not freely or adsorbed nitrogen. The reflectance of the BTiO₂ calcined at 400 and 500 °C gradually intensified as the wavelength increased. This means the absorbance was gradually weakened. The reflectance of the 600 °C sample gradually intensified as the wavelength increased to 580 nm, and then reach a plateau. Each sample of ATiO₂ had nearly identical intensities for visible absorbance at different wavelengths, furthermore, stronger visible absorbance at higher treatment temperatures was observed.

According to the defective theory, the light absorbance of the titania treated by ammonia gas was initiated by an electron located at a defective point which can absorb the visible light. TiO_{2-x} ($x=0-1$) formed while the reductive gas reacted with titania and there was insufficient oxygen in the crystal of titania. At this point, the Ti/O atomic rate changed from 1:2 to 1:2-x, as the Ti/O locality was still 1:2, thus oxygen vacancies and trivalent titanium were forming. The electron trapped by the oxygen vacancies can absorb the visi-

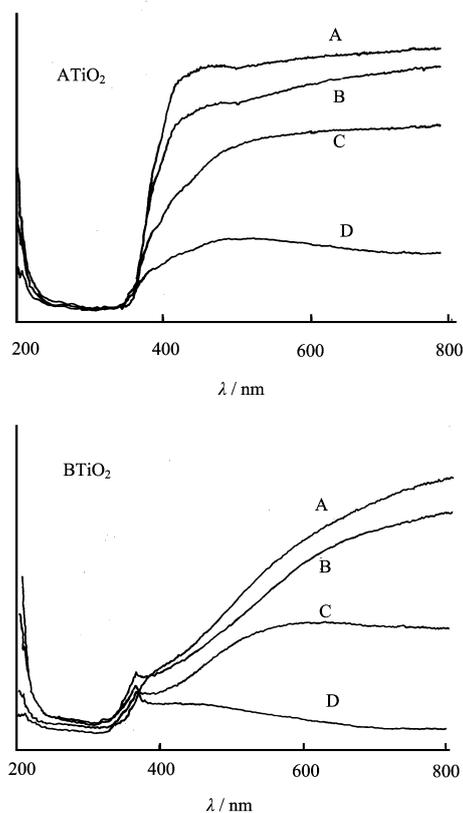


FIG. 3 UV-Vis diffuse reflectance spectra of the ammonia thermal treated TiO₂ (ATiO₂: chemical reagent purchased; BTiO₂: hydrolysis of sulfate titanium, A: 400 °C, B: 500 °C, C: 600 °C, D: 700 °C).

ble light [23]. Another explanation for the color change and visible absorbance is oxynitrides formed by nitrogen doping. Jansen reported special structure materials called oxynitrides would form in metal oxides if oxygen were substituted by nitrogen, which can absorb visible light [24]. This was verified by the XPS result. Generally, photo-absorbance is a very important factor, resulting in high photoactivity of the titania photocatalyst in a reaction. Visible light absorbance is a necessary qualification for visible light activity of the catalyst.

D. Photocatalytic activities

The photocatalytic activities of the samples were tested by oxidizing methyl orange under UV light and phenol under sun-light. The photocatalytic activities of ATiO₂ and BTiO₂ samples, calcined at different temperatures, under UV light using the methyl orange test are shown in Fig.4. For the BTiO₂ sample, photoactivity increased gradually with treated temperature, with the methyl orange photocatalytic degradation ratio gradually increasing from 29% in the 400 °C sample to 88% in the 700 °C sample. But for the ATiO₂, the samples calcined at 400 and 500 °C had almost

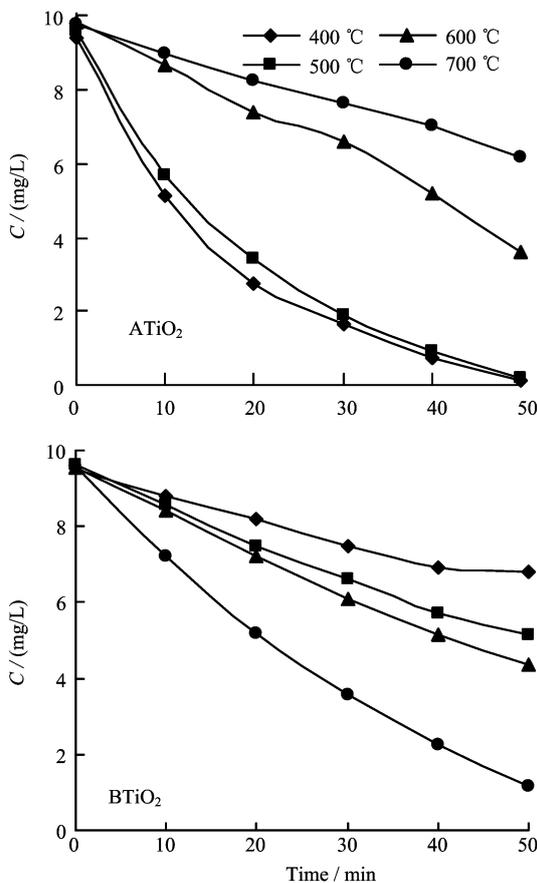


FIG. 4 The photocatalytic activities of ATiO_2 and BTiO_2 samples calcined at different temperature under UV light using methyl orange as model pollutant.

the same photocatalytic activity, however samples calcined at higher temperatures showed lower activity. After 50 min of reaction complete decolorization of the methyl orange occurred in the 400 and 500 °C samples, but only 37% color loss took place in the 700 °C sample. The opposite effects of treated temperature on the photocatalytic activity of ATiO_2 and BTiO_2 may be attributed to more than just the ammonia reduction, but also to the preparation methods. BTiO_2 was prepared by hydrolyzing titanium sulfate in ammonia solution. Sulfate and nitrogen can restrain the phase transformation from anatase to rutile as verified by the XRD results, subsequently ammonia gas treated at higher temperature can maintain the anatase, which gave high activity. Another reason for BTiO_2 's higher activity was sulfate, which can be eliminated at higher temperatures, as sulfate can block the activity site of the TiO_2 [25]. The inversion of treated temperature on photocatalytic activity suggested that the preparation conditions might be the most important factor which effects the photocatalytic activity in the system.

The results of the phenol test for photocatalytic activities of ATiO_2 and BTiO_2 samples, calcined at different temperatures, under sunlight are shown in Fig.5.

It is well known that certain UV light (UV-C, wavelength range 290-330 nm) exists in sunlight and the photo-reactive rate for this UV light is far higher than that for visible light, so eliminating this UV component is necessary for the comparison of photoactivity. As dyes or other light-sensitive organic substrates can be degraded by formation of excitation state, phenol was chosen as model pollutant [26]. Phenol cannot be degraded under sunlight without TiO_2 as a catalyst. As can be seen from the similar graphs of ATiO_2 compared to the system under UV light, the samples calcined at 400 and 500 °C have almost the same activity while the higher temperature samples showed less activity. After 120 min of reaction, about 96% of the phenol has degraded in the 400 °C sample, but only 13% in the 700 °C sample. However, BTiO_2 showed completely different results when compared to the activity under UV light, except for the 500 °C sample, which exhibited limited activity. The other three samples had almost no activity for phenol degradation under sunlight. Although visible light absorbance was high for both ATiO_2 and BTiO_2 , they still showed lower visible activities in the system. This suggested that visible light absorbance might not be a crucial factor for the ammonia gas treated TiO_2 with regard to visible activity. For the sample BTiO_2 calcined at 700 °C, we saw the highest visible light absorbance and the highest

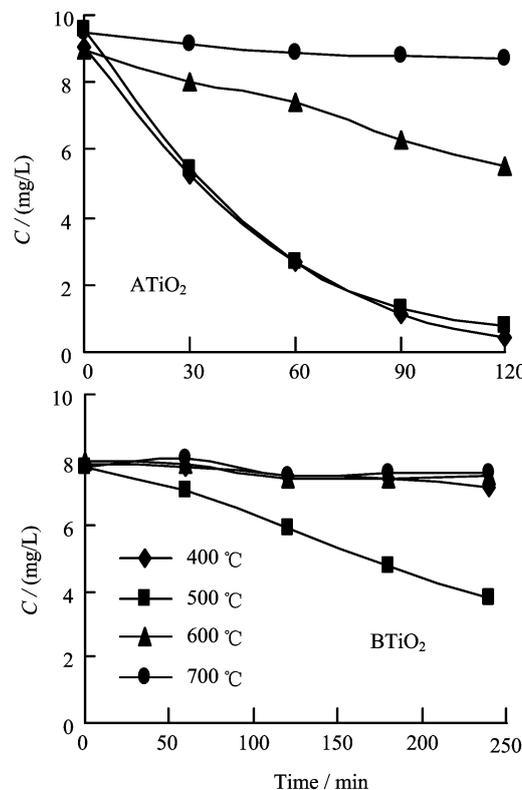


FIG. 5 The photocatalytic activities of ATiO_2 and BTiO_2 samples calcined at different temperature under sunlight using phenol as model pollutant.

activity while using UV light for methyl orange degradation, but it almost have no activity while using sunlight for phenol degradation. This suggests an electron trapped by oxygen vacancies can absorb visible light effectively but was unable to initiate visible photocatalytic reaction under the experiment conditions.

Figure 6 compared photocatalytic activity of the ammonia gas treated BTiO₂ and bTiO₂ for methyl orange degradation using UV light. Regardless of the temperature of the thermal treatment, the ammonia treated sample BTiO₂ showed lower activity compared to bTiO₂. Asahi prepared TiO_{2-x}N_x by treating anatase TiO₂ powder (ST01, Ishihara Sangyo Kaisha, Japan) in a mixed ammonia/argon (67% ammonia) atmosphere, and found the catalyst is superior to that of the TiO₂ sample irradiated in the visible range [8]; whereas both samples showed similar UV activity. Figure 7 compared photocatalytic activity of ammonia gas treated BTiO₂ and untreated bTiO₂ for phenol degradation using sunlight as irradiation source. Again, the negative photo activity of ammonia gas treatment was observed. As the various samples and light sources demonstrated, the ammonia gas treatment will show negative photoactivity for catalytic reaction. This suggests that a sample treated by ammonia gas under these experimental conditions will not be an effective or useful method for improving the activity of the TiO₂. Our findings contradict those of Asahi [8] with regard to the structure of the sample, as we found considerable unrecognized carbon on the surface of the ATiO₂ and BTiO₂. Another reason for the negative photoactivities of the nitrogen doped TiO₂ of the sample may be too high a concentration of the nitrogen on the surface of the samples.

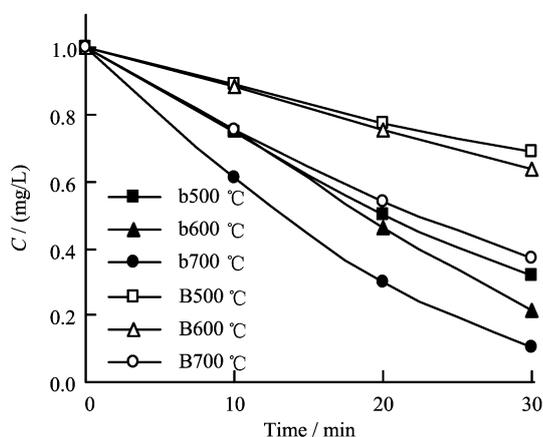


FIG. 6 Comparison of photocatalytic activity of the ammonia gas untreated BTiO₂ (hollow) and treated bTiO₂ (solid black) for methyl orange degradation using UV light.

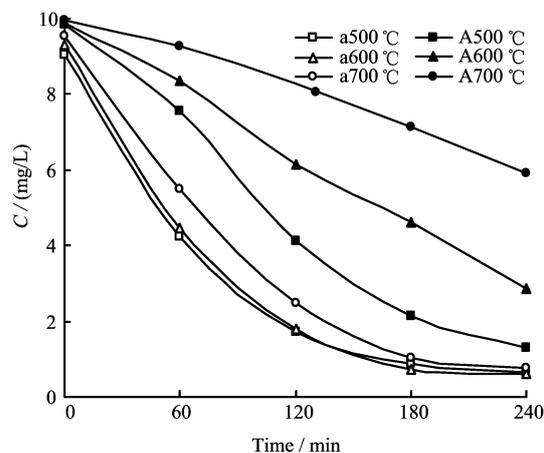


FIG. 7 Comparison of photocatalytic activity of the ammonia treated ATiO₂ (solid black) and untreated aTiO₂ (hollow) for phenol degradation using sunlight as irradiation resource.

IV. CONCLUSION

The effect of ammonia thermal treatment on two types TiO₂ were evaluated. The treated catalysts were characterized by different physical techniques and the photocatalytic activity of the samples was tested for the photocatalytic degradation of methyl orange and phenol under UV-light and sunlight respectively. The results of XRD indicated the catalyst was mainly anatase crystal phase for that prepared by hydrolyzation of sulfate titanium and a mixture of anatase and rutile for the chemical reagent. All the catalysts showed a high absorbance for visible light in the range of the experimental conditions. The visible light absorbance was attributed to the electron trapped by the oxygen vacancies or the special structure materials called oxynitrides formed by doped nitrogen. XPS results demonstrated atomic and molecular nitrogen on the surface TiO₂ existed after ammonia thermal treatment which might play important roles in affecting charge trapping and the photocatalytic behavior.

Effects of treatment temperatures on photoactivities were completely different for ATiO₂ and BTiO₂. Higher treated temperatures yielded higher activities for BTiO₂ but lower for ATiO₂. Whatever the thermal treatment temperature, the ammonia gas directly treated samples all showed lower activities (UV or sunlight) compared to the untreated one. The photocatalytic activity results suggested that the material preparation conditions might be the most important factor affecting the photocatalytic activity of the system.

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