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Graphite-based N-TiO_2 composites photocatalyst for removal of HCHO in water

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ABSTRACT

Graphite as support for catalysts has attracted a lot of attention because of its unique structure and physicochemical properties. Using graphite as substrates, the N-TiO_2/graphite photocatalyst (N-TiO_2/GC) was synthesized via a simple synthesis method that involved dip coating of substrates into an organic/inorganic sol composed of ethanol, acetic acid, tetrabutyl titanate, and faecula, followed by calcination of the coating at 400˚C. The crystal phase of N-TiO_2/GC was characterized using methods such as X-ray diffraction, UV–vis absorption spectroscopy, and scanning electron microscope technology. The photodegradation performance of the optimized catalyst was investigated using degradation of an aqueous solution of formaldehyde at different preparation conditions under visible light irradiation. The N-TiO_2/GC composites exhibited excellent photocatalytic activity, which was influenced by post-calcination temperature and the pH of the reactive system. The experimental result showed that degradation rate of the formaldehyde was 92.45% under the condition of pH 3.5 for 4 h and the natural light intensity in summer.

Keywords: Sol–gel; Graphite; Titania; Photocatalyst; Nitrogen doping

1. Introduction

In recent years, photocatalytic oxidation degradation has been shown to be a promising and effective technology for waste pollution control [1,2]. Photocatalysis can be considered the most important and new, environmentally friendly, clean chemical technology, because the pollutants can be oxidized to CO_2 and H_2O. Titania is the most effective photocatalyst and is widely applied in the fields of environmental protection such as purification of air and water. However, TiO_2 is active only within the UV light region, which accounts for a small fraction (4%) of the sun's energy, and so its activity is limited in solar light. There is an urgent need for the development of inexpensive, but reliable and efficient photocatalyst which can work under solar radiation. Thus, the goals to improve its photographic reactivity and extend its light adsorption from the UV light region to the visible light region have been pulled off and many new routes have been developed [3–6].

As doping with nitrogen is advantageous because nitrogen can be easily implanted into TiO_2 to the downward shifting of valence band maximum, the

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nitrogen-doped TiO_2 has higher photocatalytic activity in visible light regions [7]. The N-doped TiO_2-based photocatalysts with anatase-type structure were recently recognized as useful materials for achieving the objective. Asahi et al. [8] prepared N-doped TiO_2 materials that exhibited efficient visible light activity in visible regions. Belver et al. [9] had made a series of nanosized N-containing TiO_2-based materials to test their photocatalytic degradation of methylcyclohexane (MCH). It was found that these materials were characterized by high photocatalytic activity for the elimination of MCH in the gas phase under sunlight excitation. Yin et al. [10] had made N-doped titania by planetary ball milling of P-25 titania with ammonium carbonate. These TiO_2 photocatalysts were highly efficient for the destruction of methylene blue and creatinine in water.

From the previous research, it was found that the N-doped titania was an excellent photocatalyst for removing organic contaminants in wastewater or air. However, the separation of titania particles from reaction system is difficult because these particles are too fine to be removed. In order to overcome this problem, photocatalysts have been immobilized on various supported materials such as silica, glass beads, ceramics, zeolites, etc. [11–14]. Previous studies have shown that carbon doping may reduce the width of band gap of TiO_2 effectively [15], thus increasing the photocatalytic activity of TiO_2 under the sunlight excitation. Therefore, the development of new TiO_2/carbon photocatalytic materials seems to be the new target.

Several kinds of carbon materials such as carbon nanotubes, activated carbon, and activated carbon fiber were used for the advanced treatment of wastewaters, and the experimental results have shown satisfying catalytic performance [16–19]. These materials can increase the catalytic efficiency due to their good adsorption capability for pollutant molecules and its good electrical conductivity to promote the photoproduction electron to move quickly. Khan et al. [20] had used seven different carbon materials (such as activated carbons, graphite, graphitic carbon nanofibers, and so on) as supports and systematic studies for the effects of carbon materials on the TiO_2 photocatalysis. It was found that the carbon materials received great attention due to their characteristics such as large surface area (max > 1000 m^2/g), porosity, and good electrical conductivity. Therefore, these results are very important and informative in designing high efficiency photocatalysis of TiO_2/carbon composites.

Graphite has received great attention in photocatalytic materials areas (means the graphite materials have received great attention when used as photocatalysis support materials), because of its unique properties which includes high mobility of charge carriers, thermal conductivity, mechanical strength, high temperature strength, and specific surface areas. Jiang et al. [21] synthesized graphite oxide/TiO_2 composites as a highly efficient photocatalyst by *in situ* deposition of TiO_2 nanoparticles on graphene oxide nanosheets. The composites exhibited excellent photocatalytic activity. The photooxidative degradation rate of methyl orange was 7.4 times higher than that of P-25 TiO_2.

The low-density synthetic polycrystalline graphite has specific surface areas and adsorption capacity similar to that of the active carbon. And, its mechanical machining property makes it suitable for use as an excellent support material in industrial application. However, the use of the polycrystalline graphite in photocatalytic materials areas has not been heard up to the present. Therefore, a new way of preparing N-TiO_2/graphite (N-TiO_2/GC) composite by dipping the graphite into the intermixture composed of the N-TiO2 and fecula solution which could achieve stronger binding between TiO_2 and graphite was proposed and the photocatalytic activity of the N-TiO_2/graphite was investigated under visible light in the paper.

2. Material and methods

2.1. Materials and reagents

All chemicals used in this study were received from Shanghai Chemical Regent Factory of China without further purification. The $Ti(OBu)_4$, urea, ethanol, and acetum were analytical reagents and distilled water was used throughout the work. The concentration of formaldehyde was 20%. The synthetic graphite (pure, 99.9%, density, 1.23 g/cm^3) was obtained from Pingdingshan Dongfang Graphite Co. Ltd. China.

2.2. Preparation of photocatalysts

The N-doped TiO_2 nanocomposites powders were prepared via the sol–gel method. To obtain Solution A, 15 mL (0.04 mol) tetrabutyl titanate was dissolved in 45 mL ethanol. Urea with different ratios of N and Ti (mol ratio = 1:1, 1:2, 1:3) was then dissolved in 20 mL, 20% acetum to obtain homogeneous Solution B. The pH of the solution was adjusted to 2–3 by adding nitric acid (1 mol/L). Thereafter, Solution A was added dropwise into Solution B at room temperature with strong agitation for 1 h to get the sol. The sol was left at room temperature for 6–8 h in order to solidify to form the gel. Then, the gel was dried in an oven at 80℃ for 1 h and was calcined at 400℃ in muffle furnace for 2 h to obtain N-TiO_2 powder.

Using graphite as carrier, the N-TiO_2/graphite (GP) film photocatalyst was synthesized via a simple dip-coating method that involved dip coating of appropriate substrates into an organic/inorganic sol composed of ethanol, acetic acid, tetrabutyl titanate, urea, and faecula. After the sol was left at room temperature for 6 h to get the gel, it was followed by calcination of the coating for 2 h at different temperatures (400, 450, and 500℃) in muffle furnace.

2.3. Characterization of photocatalysts

X-ray diffraction (XRD) patterns of the N-TiO_2/GP were obtained using a Rigaku D/max-2550PC diffractometer. Both particle size and shape of the co-doped TiO_2 composite photocatalyst were tested using a Hitachi H-800 transmission electron microscope. UV–vis diffuse reflectance spectra (UV–vis DRS) were recorded in the wavelength range of 200–800 nm using PELAMBDA35 spectrophotometer. Absorption spectra were referenced to $BaSO_4$.

X-ray photoelectron spectroscopy (XPS) measurements were performed with the PHI1600 Quantum ESCA Microprobe System, using the Mg K. Line of a 300 W Mg X-ray tube as a radiation source at 15 kV voltages. All the binding energies were referenced to the C 1s peak at 284.8 eV of the surface adventitious carbon.

2.4. Photocatalytic activity measurements

A set of photocatalytic degradation experiments in aqueous formaldehyde solution was performed with the following procedure: prior to photoreaction, the formaldehyde solution with an initial concentration of 10 mg/L was magnetically stirred in the dark for 30 min to reach adsorption–desorption equilibrium; then, the reaction mixture was irradiated by the natural light intensity in summer from the top vertically. During the photoreaction, samples were drawn from the reaction suspensions at a time interval of every 30 min and centrifuged at 9,000 rpm for 5 min, and then filtered through a 0.2 μm Millipore filter to remove the particles. The formaldehyde concentration changes of the filtrates were analyzed by UV spectrophotometer (722 N) by measuring the absorbance of formaldehyde solution (phenol reagent spectrophotometry) at its maximum absorption wavelength of 630 nm during the whole irradiation time. The doze of powder catalyst added was 2 g/L and the clinker catalyst added was 6 g/L. Visible light photocatalytic activities of the photocatalysts were measured by the decomposition rate of formaldehyde in an aqueous solution at ambient temperature in summer. The formaldehyde degradation rate was calculated by the absorbance change.

3. Results and discussion

3.1. Catalyst characterization

The XRD was used to investigate the phase structures and average crystallite size of the N-TiO_2 nanocomposites photocatalyst, and compare the XRD patterns with that of the N-TiO_2, N-TiO_2 /GP, and the Degussa P-25 TiO_2. It can be seen that well-crystallized anatase N-TiO_2 was formed without contamination of any other crystalline phases in the Fig. 1. No other phases such as rutile or brookite and TiN were observed in all the samples. The anatase phase was evidenced by the characteristic diffraction peaks of anatase (major peaks: 25.22°, 37.87°, 48.12°, and 54.2°) in the XRD spectrum of each sample [22]. When the P-25 TiO_2, N-TiO_2, and the N-TiO_2/GP powders were compared, it was found that the diffraction peaks of TiO_2 changed, indicating that N was doped in TiO_2. When the N-TiO_2 and the N-TiO_2/GP powders were compared, the peaks of C were not observed. This may be due to the C in $\theta = 25^\circ$ characteristic peak which were covered by the anatase TiO_2 characteristic peak ($\theta = 25.2^\circ$) and the peak of the graphite in 43.4° which were weak peaks.

From the scanning electron microscope (SEM) image (Fig. 2), most amorphous particles were observed on the surface of the graphite (a). In addition, some lacunaris TiO_2 films were found on the outer layer of the graphite (b), which could improve the absorption property of the new photocatalyst. This is because the faecula were changed to the active carbon when it was calcined at 400℃ to form the porous carbon layer.

The chemical state and the concentration of nitrogen atoms in the N-doped TiO_2 were investigated by XPS. As shown in Fig. 3, it can be seen that the XPS survey spectrum of commercial TiO_2 does not include a centered peak at 396 eV. It was obvious that the binding energy around 396 eV which related to the existence of N–Ti binding could be observed in the N-doped TiO_2, although the peak intensity was not so strong, it was in accord with the result of the reference [9]. The total N concentrations calculated from the XPS spectra were 2.2%.

Fig. 4 illustrated the diffusion reflectance spectra of P-25 TiO_2, N-doped TiO_2, and the N-TiO_2/GP powders. The P-25 titania showed an absorption edge at 408 nm corresponding to the band gap of 3.04 eV (Fig. 4(a)). It can be seen that the doped photocatalysts

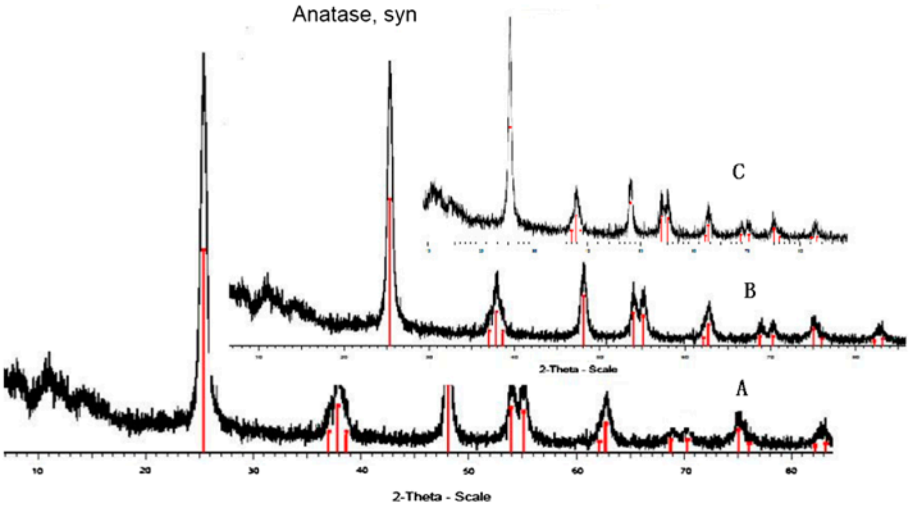
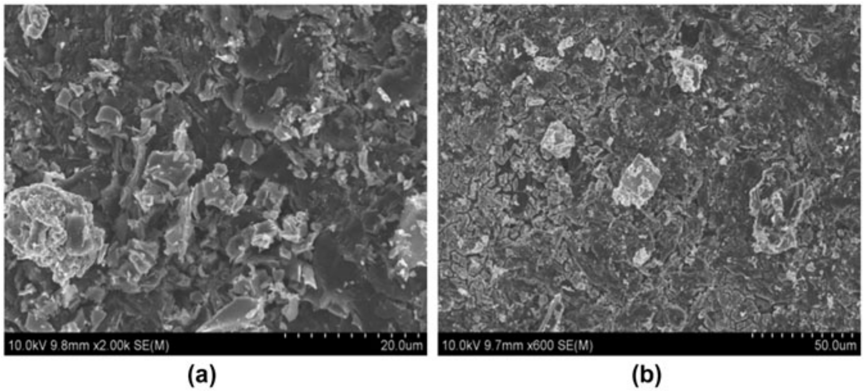


Fig. 1. XRD patterns of as-prepared (A) TiO_2, (B) N-TiO_2 composite, and (C) N-TiO_2/GP after calcination treatment at 400˚C for 2 h, where the crystalline orientation of anatase was shown.



(a) (b)

Fig. 2. SEM images of heat-treated graphite N-TiO_2 composites.

have some absorption in the range of visible light ($\lambda > 400$ nm), and the absorption edge showed an obvious red shift with the N, C insert in the crystal structure, which could be ascribed to the C, N doping changes to the broad bandwidth of the Ti–O. The powders of N-doped TiO_2 and the N-TiO_2/GP showed two absorption edges at 495 nm and 504 nm (Fig. 4(b)–(c)), respectively. Asahi et al. [8] believed that the appearance of new absorption band was due to the formation of isolated levels that consisted of N 2p orbitals in the band gap of TiO_2. Because of the yellow color of the calcined N-TiO_2 and white color of nondoped sample, the absorption measurement of calcined N-TiO_2 showed stronger photoabsorption in the range of long wavelengths compared with the nondoped TiO_2.

We ascribe the mechanism through which the visible light photocatalysis of N-containing TiO_2 powders is enhanced through the addition of C to the synergistic effect of N-doping and N-TiO_2/GP coupling. When the N, C insert in the crystal structure was performed, a new electronic impurity level (EIL) is formed. The photogenerated electrons in the Ti could first have been excited to the EIL, and then transferred to the N by absorbing more energy in the first step transition. Then, electron transition from N to O in an N-TiO_2 semiconductor can be achieved through two-step transitions even with the lower energy of visible light irradiation since an EIL is formed. And, the C has the same mechanism in the crystal structure. The C has more electrons holes and delays the recombination of photogenerated electrons.

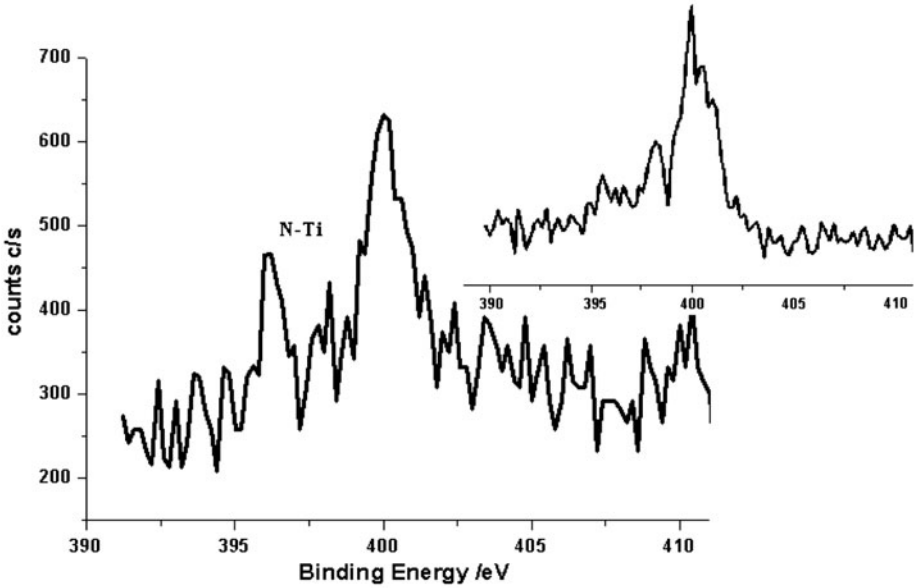


Fig. 3. XPS spectra of N 1s peak for N-TiO_2/anatase samples.

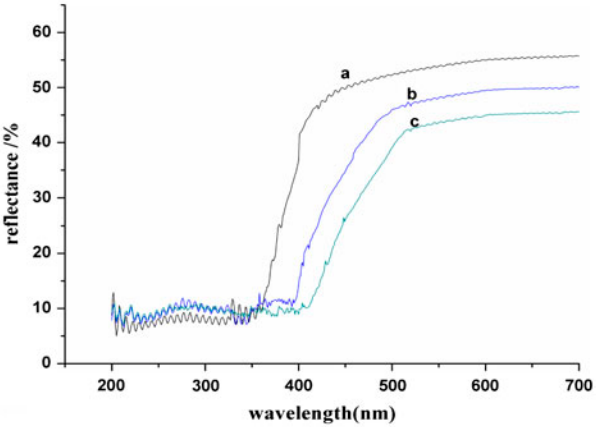


Fig. 4. UV–vis diffuse reflectance spectra of bare TiO_2, N-TiO_2 composites, and N-TiO_2/GP.

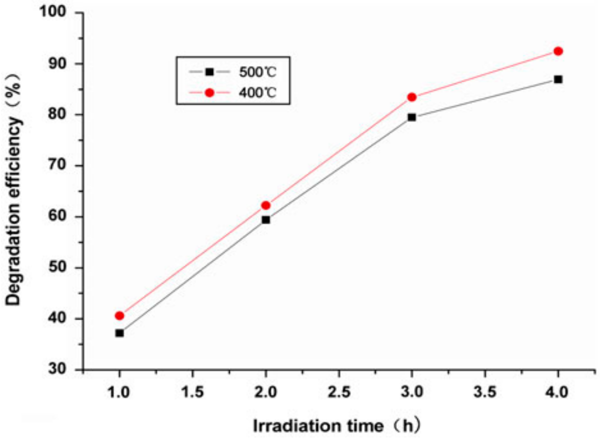


Fig. 5. Photocatalytic activity of the N-TiO_2/GP photocatalyst shiver calcined at different temperatures for degradation formaldehyde.

3.2. Photocatalytic activity studies

3.2.1. Effect of the preparation condition

Heat-treatment temperature has great influence on phase transformation of TiO_2, and has a significant effect on the activity and stability of the catalysts sequentially. The photocatalytic activity of the synthesized N-TiO_2 obtained at different heat-treatment temperatures and activation times were observed.

As shown in Fig. 5, N-TiO_2 powder calcined at 400℃ for 2 h showed the highest photocatalytic activity with the degradation formaldehyde solution. Increasing the calcination temperature to 500℃, the photocatalytic activity decreased significantly, and this could be attributed to the physical property of N-TiO_2 photocatalyst powders which changed greatly. Compared with the reference [23] calcined at 450℃ for 6 h in air and that calcined at 400℃, the later may reduce the preparation time, and get better results. The composite was dried in an oven at 400℃ in order to avoid any physicochemical changes of the carbon materials that could occur at higher temperatures in the presence of oxygen at the same time.

The photocatalytic activity of the N-TiO_2 nanocomposites with different molar ratios of N and Ti calcined at 400℃ for 2 h is shown in Fig. 6. The ratio of N and Ti was changed to obtain titania with different nitrogen contents namely, N-doped (1:1), N-doped (1:2), and N-doped (1:3). The photocatalytic activity of all the three synthesized photocatalysts was evaluated for formaldehyde degradation. It can be seen that the highest percentage degradation was observed in case of the N-doped (1:3). The higher activity of these photocatalysts was attributed to the nitrogen doping. Therefore, the N content should be an important factor affecting the photocatalytic activity of the N-TiO_2 nanocomposites photocatalyst. But, further increase in the N content led to a decrease in the photocatalytic activity of the N-TiO_2 nanocomposites photocatalyst. This could be due to the high level of nitrogen doping that made high defects density leading to poor photocatalytic activity. Therefore, for the N-TiO_2 photocatalyst, the maximum photocatalytic activity appeared when the molar ratio of N and Ti was 1:3, calcined at 400℃ for 2 h.

3.2.2. Effect of various parameters on photocatalytic degradation

The effect of catalyst loading on photocatalytic degradation of formaldehyde by N-TiO_2/GP was studied. The N-TiO_2 loading on graphite was varied from 1.37%w/w (dipping one time) to 3.9%w/w (dipping three times). The increasing degradation rate of formaldehyde was varied from 87.2, 92.3 to 85.4%. Therefore, it can be seen that when the catalyst loading was increased further to 3.9%w/w, the rate of degradation decreased slowly. The decrease in degradation rate with the increase in catalyst loading can be attributed to the decreased amount of the hole in layer of the graphite which hinders the adsorption capacity for the pollutant.

The pH of the reactive solution is an important factor which affects the formaldehyde degradation rate. The influence of pH on the photocatalyzed degradation of formaldehyde was investigated at various pH levels (3.0–10.0) with constant pollutant concentration and photocatalyst amount. In acidic range, the pH was varied using 0.1 M HCl, while in alkaline range, the pH was varied using 0.1 M NaOH.

It was found that the formaldehyde degradation was effective at lower pH and showed a higher degradation rate at weakly acidic conditions (pH ranges approximately from 3.01 to 7.02) in the Fig. 7. The reason for this may be ascribed to the formation of HO_2^- oxidant in the presence of H^+ by the reaction equation of $H^+ + O_2 + 2e \rightarrow HO_2^-$, which facilitates reactive formaldehyde oxidation under weakly acidic or neutral conditions.

3.2.3. Photocatalytic activity on the degradation of formaldehyde

The natural sun light during the five months at noon over the quartz glass reactor was used as light source. The photocatalytic activity of the synthesized N-TiO_2/GP was evaluated with the degradation of formaldehyde under irradiation of visible light.

From Fig. 8, it is evidenced that N-TiO_2 presented the better photocatalytic property compared with pure TiO_2. These findings are consistent with the previous results [21]. The N-TiO_2 powder catalyst displayed higher degradation capability for formaldehyde under visible light irradiation, whereas N-TiO_2/GP showed the best degradation capability at the same visible

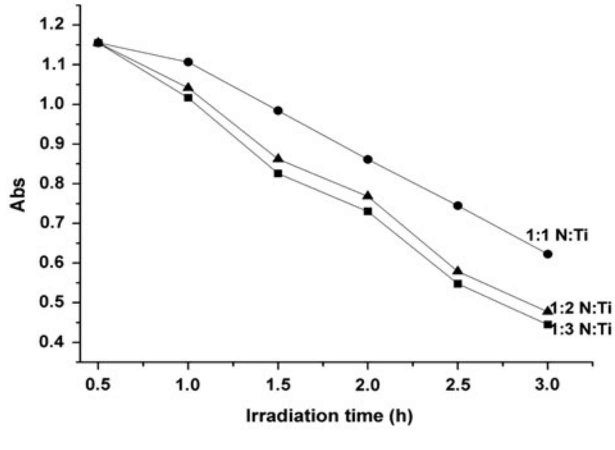


Fig. 6. Photocatalytic activity of the N-TiO_2 photocatalyst with different molar ratios of N and Ti for the degradation of formaldehyde.

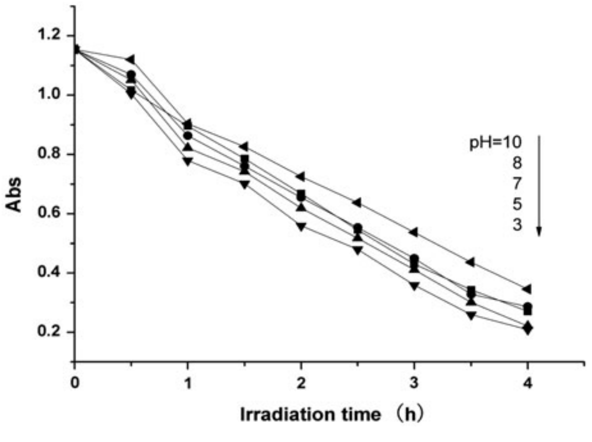


Fig. 7. Effect of initial pH on the formaldehyde degradation.

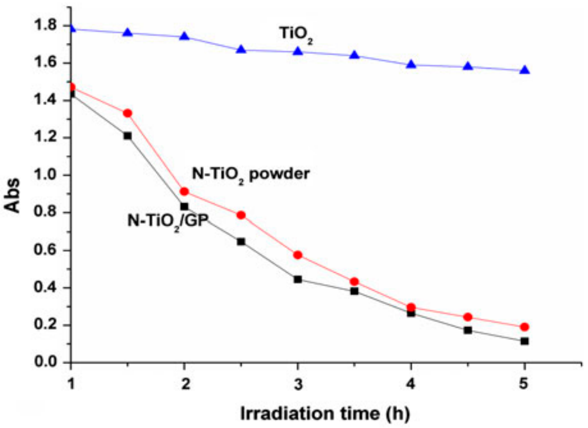


Fig. 8. Photocatalytic activity of various samples for formaldehyde elimination under irradiation of visible light (λ > 400 nm).

light irradiation condition. The degradation rate of the formaldehyde was achieved at 92.45% in 4 h at pH 3.5 under the natural light intensity in summer. The variation of photocatalytic performance of N-TiO_2 and N-TiO_2/GP can be attributed to the morphologies as observed by SEM in Fig. 2. The active carbon formed from the calcined faecula on the graphite outer layer can improve the amount of crystalline nanocrystal facets and enlarge the adsorption capacity of the N-TiO_2 powder which leads to better photocatalytic performance than the other samples.

Although the light intensity has not been measured, the data of degradation efficiency of formaldehyde in different intensity of the sun were obtained in the experiment (in different weather conditions such as sunny, cloudy and so on). And, the results displayed that the degradation efficiency of formaldehyde is higher in sunny day than cloudy (the date are not shown).

4. Conclusion

The novel N-TiO_2/GP photocatalysts were prepared with the simple dip-coating method. The characteristic patterns of XRD, TEM, and UV–vis diffuse reflectance showed that the N-TiO_2/GP photocatalysts calcined at 400℃ for 2 h (with the molar ratio of N and Ti is 1:3) were found to have better crystallization, smaller crystal size, and had some response for visible light (λ > 400 nm). The absorption spectra of N-doped TiO_2 were expanded from about 400 nm to about 500 nm, which would greatly enhance the utilization ratio of visible light in solar spectra. The effects of heat-treatment temperature and N/Ti mole ratio in photocatalyts properties were studied. The anatase type of TiO_2 was obtained and photodegradation studies for formaldehyde were carried out (N-TiO_2) under visible light radiation. The N-TiO_2/GP photocatalysts displayed much higher activity under visible light. From the results obtained in this study, it can be concluded that synthetic polycrystalline graphite has good adsorption capacity and can be used as support for powder photocatalysts and expand its use in the field in practical application.

Acknowledgments

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