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MRes in Sustainable Building Technology

**Fe/N Co-doped TiO₂ Loaded on Functionalized Activated
Carbon Fiber for Photocatalytic Removal of Formaldehyde**

By

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Research**

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Abstract

An improved sol-gel method was used to synthesize a new type of photocatalyst Fe/N co-doped TiO₂ supported on functionalized activated carbon fiber (ACF), which was applied to catalytically degrade the formaldehyde in the visible light region. The samples were improved by adjusting the amount of hydrolysis water, calcination temperature variation, different pretreatment method for functionalization of ACF and employing different concentration of sodium dodecyl benzene sulfonate (SDBS), which was used as the surfactant for TiO₂ particles with a high formaldehyde degradation efficiency up to 75.6% in 120 mins, was obtained. The prepared photocatalysts were characterized via X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and Brunauer-Emmett-Teller specific surface analysis (BET). The SEM analysis showed that TiO₂ particles were dispersed uniformly on the surface of ACF. The particles exhibited the anatase structure is the main crystalline phase and rutile also existed with the crystallite diameter of 19.5 and 24.1 nm, respectively. In general, this photocatalyst can degrade low concentration of formaldehyde gas with great efficiency under visible light irradiation which is fit for the application of indoor formaldehyde degradation.

Keywords: Photocatalytic degradation; Codoped ACF/TiO₂; Formaldehyde; Visible-light irradiation

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Chapter 1. Background And Literature Review

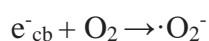
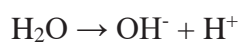
1. Background

Indoor air purification has received wide attentions since the 1890s. It is known that people generally spend 80% of their time indoors, where air quality can be worse than in the ambient atmosphere due to the various emission sources in the indoor environment. Formaldehyde is not only a main compound in the group of volatile organic compounds (VOCs) in the outdoor atmosphere, but also one of the most notorious indoor air pollutants. It mainly comes from cabinetry, plywood floor and other furnishings in a house. Formaldehyde exists in gaseous phase at room temperature, which is a colorless and highly oxidative irritant and smelly gas. Through both short-term and long-term exposure to HCHO (Formaldehyde) containing air (for instance, its concentration exceeds the healthy threshold), people may suffer a variety of acute or chronic symptoms/illnesses including headache, dizziness, feebleness, sensory disturbance, immunity decrease, somnolence, hypomnesia, neurasthenia and depression, or even probably respiratory dysfunction and toxic liver damage including hepatocellular injury and liver radiant energy abnormalities.¹

Since the life quality of human beings has been continuously improved due to industrialization and urbanization, more and more concerns regarding to the air quality and relevant safety issues in the indoor environment have been raised. From the published literatures, a number of techniques or processes such as adsorption, filtration and oxidation have been reported on how the formaldehyde could be removed indoors. Among them, photocatalytic oxidation seems to be a cost-effective and environmental-friendly solution to reduce the formaldehyde concentration in an indoor environment. However, challenges of further significantly improve the efficiency of formaldehyde degradation by photocatalyst still remains²⁻³

Till now, many efforts have been made to degrade indoor gaseous formaldehyde via photocatalysis, especially TiO₂.⁴⁻⁷ But catalyst mentioned above can't effectively degrade formaldehyde under visible light.⁷ In addition, the other catalysts can successfully degrade formaldehyde under visible light, but can just degrade formaldehyde gas with 1 mg/m³ (equal to 1.33 ppm) and failed to degrade formaldehyde with higher concentration which means this catalyst can only deal with formaldehyde gas with low concentration.⁵ Therefore, the screening of the photocatalyst that is capable of degrading HCHO within visible light spectrum is expected to be more promising.

Under the irradiation of UV, the electron (e⁻) in TiO₂ can be excited from valence band (VB) to the conduction band (CB). The motivated electrons are then trapped by O₂ which is adsorbed on the catalyst surface and then produced O₂^{-•}. After a series of reaction, formaldehyde molecules are finally degraded into CO₂ and H₂O.⁸



The holes and electrons react with OH⁻ and O₂^{-•} molecules on the catalyst surface to form ·OH radicals and O₂^{-•} superoxide radicals, respectively. Then HCHO will combine with ·OH and become ·CHO free radical. ·CHO will trap O₂^{-•} and finally produce HCOOH. HCOOH then react will reactive oxygen radicals and degrade into H₂O and CO₂.⁹

2. Literature review of photocatalytic degradation of formaldehyde using different types of catalysts

In recent years, research on formaldehyde degradation photocatalysis mainly concentrates on semi-conductive materials made of metallic oxides or metallic sulfides, among which TiO₂, ZnO, SnO₂ and WO₃ have been under the limelight of broad study as model materials due to their outstanding merits, such as strong oxidative capacity, high photocatalytic activity, low cost and non-toxicity .¹⁰⁻¹³

2.1 Titanium dioxide (TiO₂)

The energy band structure of TiO₂ particle consists of a low energy valence band and an empty high-energy band. The gap width between the valence band and the guide band is 3.2eV. When nano-structured TiO₂ particle is exposure with a light with energy larger than the wide of band gap, electrons in the valence electrons will be motivated to conduction band, and thus, forms electron-hole pairs. The electron-hole pairs will charge TiO₂ and degrade organic matter into CO₂ and H₂O.^{9, 14}

Li et al.¹⁰ prepared a doped titanium dioxide photocatalyst by the sol-gel method, and was characterized by techniques such as XRD, SEM, TEM etc. Using formaldehyde as the simulated pollutant, the photocatalytic activity of the catalyst was explored, and the impacts of different concentrations of formaldehyde and of different bonding agents on the photocatalytic efficiency were discussed. The results are summarized as the followings: 1) the higher initial concentration of formaldehyde within the concentration range from 0.5-1.0 mg m⁻³, the higher degradation efficiency up to 80% will be achieved during the first 3 hours when the photocatalysis occurred under UV light. 2) Among different substances such as sodium alginate, deionized water, and pure acrylic latex, which are often used for bonding agent, sodium alginate was the best candidate only maximize the degradation efficiency of formaldehyde, but also bring a better bonding performance.

Cheng et al.¹⁵ prepared nano-titanium dioxide by low-temperature hydrolysis, and was characterized by SEM and XRD. Such nano-titanium dioxide was made as

photocatalysis coating, and its formaldehyde degradation was studied. By taking the degradation rates of formaldehyde in a vessel as references for comparison, the impacts of photocatalysis coating on the degradation rate of formaldehyde under different loading capacities, different temperatures, and different humidities were investigated. The results showed that the degradation rates of formaldehyde in the photocatalysis coating, which was made in a system where 5 g of nano-titanium dioxide was loaded onto 200g of latex, could reach a value of 93% at the experimental conditions 25 °C, 50 % humidity, and 120 min of exposure to ultraviolet radiation. This result was much better than the performance of the commercial available P25 nano-titanium dioxide.

Lin et al.¹⁶ prepared a kind of composite fabric that can degrade formaldehyde. Firstly, the Ag, Fe-codoped modified titanium dioxide was prepared, and then the Ag-Fe-supported composite fabric of titanium dioxide was prepared by the impregnation-baking-calcining method. Secondly, the prepared photocatalyst material characterized by SEM and UV-Vis. Finally, with a visible-light high-pressure mercury lamp as the light source, and taking the formaldehyde as the degradation target, the subsequent photocatalytic performance was studied. The results showed that the silver and iron element significantly changed the UV-Vis DRS data sample of the catalytic materials. The greater the amount of doped metal elements, the stronger the visible-light absorption ability of the composite catalytic material will be. In addition, the formaldehyde purification ability of the catalytic material under visible light was enhanced by the addition of silver and iron elements . The most optimum doping amount of silver was 1.5% and that of iron was 1%.The TiO₂ is able to completely catalyze the degradation of of HCHO into CO₂ and H₂O without introducing any potential intermediate hazardous pollutants during the entire reaction¹⁷.

Although TiO₂ based photocatalyst possesses some outstanding features in formaldehyde photocatalysis, some limitations and technical hurdles still remain to be overcome: (1) the photo-catalytic activity of TiO₂ is limited by its low adsorption property, (2) a high recombination rate of the photo-excited electron-hole pairs within nanoseconds, causing low quantum efficiency of the catalyst and (3) a large energy

band gap¹⁸⁻¹⁹.

2.2 Zinc Oxide (ZnO)

ZnO itself cannot degrade formaldehyde. Instead, with the aid of light source of specific wavelength, it acts as a photocatalyst to degrade formaldehyde. Also, photocatalytic oxidation technique has been put into wide application in fields of energy, chemical industry and environmental protection, thus becoming a hot research topic.²⁰

Fang et al. have produced ZnO modified by a mixing of Sn, Ag and Al, and have studied its effectiveness of degrading formaldehyde in water. The results indicate that ZnO mixed with Sn and Ag show a better photocatalytic activity than that of pure ZnO. As the original concentration of formaldehyde increases, its degradation rate decreases. Likewise, as the amount of photocatalyst and reaction duration increase, the degradation rate of formaldehyde will increase accordingly with compromising reaction speed being slowing down the²¹

Long et al. prepared nano-ZnO by hydrothermal method, and its structure was characterized by SEM and XRD method. The self-made nano-ZnO was then added into photocatalytic coating and evaluated by the degradation rate of formaldehyde in the reactor. The effects of charge number of nano-ZnO, temperature and humidity to the degradation rate of formaldehyde of photocatalytic coatings were studied. The research results indicated that degradation rate of photocatalytic degradation of formaldehyde achieved 88% after irradiated with UV for 150 mins with experimental condition being kept as the followings: reaction temperature 25°C , the humidity 50%, and charge number of nano-ZnO 6g.¹¹

2.3 Stannic Anhydride (SnO₂)

SnO₂ is a kind of powder with the structure of square rutile. It is insoluble in water and is stable with acids and bases, but when heated together with strong base, it would produce soluble stannate. SnO₂ is an excellent transparent conductive material due to its excellent conductivity, light-shielding, fire-resistance and chemical stability. It is

also the first transparent conductive material that has been commercialized. As a new functional material, SnO₂ has been found for wide application in fields like semiconductor, gas-sensitive material, transparent conductive material, optical glass, luminescent material, functional ceramic, and solar cell.²²

At present, the research on the photocatalytic capacity of SnO₂ mostly concentrates on nano-crystal size and mixing SnO₂ mixing with oxides like ZnO and TiO₂²³, while the reports on effect of SnO₂ nano-crystallized structures upon photocatalytic performance are still very limited. Dai and others²⁴ have fabricated SnO₂ nano flowers within a SnCl₄·5H₂O-HF-H₂O hydrothermal system. The comparative photocatalytic capacity study in the degradation of Rhodamine B using prepared SnO₂ nano flowers, the SnO₂ nanoparticles and commercial TiO₂ nanoparticles was conducted. The results indicate that the photocatalytic capacity of the prepared SnO₂ nano flowers show the best performance on the degradation of Rhodamine B. The enhanced photocatalytic capacity from the prepared SnO₂ nano flowers comes from the improved specific surface area of the nanostructure, which provides more active ends for adsorption and desorption on the surface of catalyst.²⁵

Wu et al. prepared SnO₂ nanoparticles via a novel and effective method. Firstly, the high-temperature which was made by electric was used for the sublimation of tin on the reaction stage. Meanwhile, the other side of the reactor would collect the nanoparticles of tin via high voltage electric. Then the nanoparticles was treated by 800°C-900°C in air atmosphere and finally obtained the SnO₂ nanoparticles. The particle size of self-made SnO₂ nanoparticles was 50nm with few impurities within the prepared nanoparticles. The SnO₂ nanoparticles was then used for photocatalytic degradation of formaldehyde. The results showed that the degradation rate could achieve 1.264mg/kg h.¹²

2.4 Tungsten Trioxide (WO₃)

WO₃ is an effective catalyst for visible light. It is a yellow powder whose shade of color varies with particle size. It shows excellent catalytic capacity as to most reactions

including oxidation, hydrogenation and dehydrogenation, hydrocarbon isomerization, and alkylation²⁶. Its band gap is 2.5-2.8 eV, mainly absorbing lights with wavelength less than 443 nm. It is highly stable in this sense and has wide optical absorption band. Because WO_3 possesses very alluring features such as efficient degradation of organic pollutants, cost-effectiveness in availability, less environmental impact, it shows prosperous future for indoor pollutant remediation when ultra violet are not available.

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Zou et al.¹³ used sodium tungstate as raw material to fabricate tungstic acid with the series of different techniques from cation resin exchange, hydrothermal method, anodic aluminum diaphragm method, ultrasonic cavitation-centrifugation method, and microwave radiation circumfluence method to fabricate sets of WO_3 products. WO_3 thus acquired has been used to degrade gaseous formaldehyde through photocatalysis and its photocatalytic capacity has been assessed. The performances of photocatalytic capacity of these WO_3 prepared under different approaches were rated as the followings: microwave radiation circumfluence method > ultrasonic cavitation-centrifugation method > hydrothermal method \approx anodic aluminum diaphragm method. Under UV lights, $\text{WO}_3 \cdot 0.33\text{H}_2\text{O}$ NiO fabricated by microwave method degrades formaldehyde by photocatalysis perform a degradation rate 3-4 times of that sample fabricated by sol-gel method. The results showed that degradation rate of $\text{WO}_3 \cdot 0.33\text{H}_2\text{O}$ NiO fabricated by microwave method is 76.8%. After five consecutive uses, this catalyst did not show obvious deactivation.

Bai et al.²⁸ used microwave method to prepare NiO/ WO_3 photocatalyst. The structure and its morphological of the photocatalyst were characterized by the followings: XRD, TGA, electron microprobe and UV-vis. The photocatalytic activity and stability were then evaluated. The results showed that the photocatalyst prepared by microwave method possessed a few better features such as the higher crystalline, smaller crystal size, higher specific surface area and higher stability, than the catalyst prepared from conventional method. When the doping amount of NiO was 1%, photocatalytic activity achieve its peak at 85.4% in 120mins.

3. Catalyst Supports

Photocatalysts carrier is the support of primary catalysts and cocatalysts . In order to enhance photocatalysts' catalytic activities, thermostability, specific surface area and pore structure of the carrier should be considered when loading photocatalysts onto the carrier. A favorable carrier can enhance dispersion degree of active components, improve catalytic activities and thermostability of active components of photocatalysts. Recently, variety of materials with porous structure and low air resistance such as, polyester particulate filter, porous cellulose fiber, zeolite molecular sieve, activated carbon and porous ceramics have been published to be used as support to load photocatalysts for formaldehyde degradation .²⁹

Zeolite molecular sieve (ZMS) is a kind of hydrated aluminium silicates with 3-D polyaninoic structure. Due to the large specific surface and good adsorption capacity, ZSM can be used as catalyst carrier to improve catalytic performance. Yang et al. ³⁰ used ZSM-5 as the carrier to prepare MnO₂/ZSM-5 via impregnation method. It was found that the enhanced degradation of HCHO by promoting concerted reaction O₃ and catalytic efficiency were achieved. . The maximum catalytic efficiency of 87% was achieved with the duration running up to 120 hours, when the ratio of MnO₂ and ZSM-5 is 1 to 10.

Zhang et al.³¹ prepared a kind of composite photocatalyst material by taking self-made nano-titanium dioxide as the main catalyst and perhafnate as the carrier. Formaldehyde and ammonia were used as simulated experimental samples, and the impacts of composition, absorption, and light conditions of the material on the degradation efficiency of formaldehyde and ammonia were investigated. By film formation preparation technique with a ratio of 8:2 (perhafnate/ self-made nano-titanium dioxide), an obvious improvement of photocatalytic degradation of formaldehyde and ammonia was observed. In addition, when the catalytic material was placed farther away from the light source, the catalytic efficiency of the catalytic material can be significantly improved by optical fiber.

By using 6% sulfated palygorskite as a carrier, Li et al.³² screened the active

components in the attempt of removing formaldehyde by various metal oxide using impregnation methods.. The best catalyst with the particle sizes in the range of 40~60 mesh was achieved under the following experimental conditions: the catalyst was treated catalysts at 300 °C for 4 hours with a manganese nitrate content of 9% ..The optimal experimental conditions for the preparation of MnO-supported palygorskite adsorption-oxidation catalysts were achieved by the orthogonal test. The results showed that, with an initial formaldehyde concentration of 9.5552 mg m^{-3} in the air, the adsorption capacity and removal rate of formaldehyde were around 0.188 mg g^{-1} and 98.35%, respectively, in the first 24 hours. The palygorskite-supported manganese oxide was then characterized. The IR absorption peak of formaldehyde was at 3420.73 cm^{-1} , and it was originally believed that formaldehyde was degraded into carbon dioxide and water by using manganite; however, XRD showed that the crystal form of manganite was changed from a cubic shape into an inclined shape after the absorption. It was presumed according to the changes in the crystal form that the manganite was closer to Mn_2O_3 before the absorption, but was then closer to MnO_2 after the absorption. Wang et al.³³ prepared the acrylonitrile-vinylidene chloride copolymer fiber containing activated carbon loaded nano- MnO_2 in the laboratory. The fiber was applied to adsorb and decompose formaldehyde at room temperature. The experimental result shows that, the MnO_2 microparticles scatter uniformly with an average diameter of 300 nm after grinded for 6 hours. This indicates the loading of the surface of fiber in flat was successful. The removal efficiency of formaldehyde by prepared catalyst reached up to 94.07% after 72 hours. The addition of N atom, N-dimethyl formamide (DMF) into catalyst matrix also improves the efficiency.

Yu et al.³⁴ compared and studied absorption and degradation characteristics of diatomite and diatomite-based nano- TiO_2 during photocatalytic degradation of formaldehyde. With the variation of the initial concentration, reaction temperature, illumination intensity, and relative humidity of formaldehyde in a reactor, the degradation of diatomite-based nano- TiO_2 photocatalyst into gaseous formaldehyde with a coating amount of 62.5 g m^{-2} was studied. The results showed that the effect of formaldehyde absorption imparted by diatomite was limited to only a certain extent, while diatomite-

based nano-TiO₂ photocatalyst provided continuous absorption and degradation of formaldehyde. The higher the initial concentration of the formaldehyde in a reactor, the longer the degradation time will be. The degradation rate of gaseous formaldehyde with an initial concentration of $6.0 \times 10^{-3} \text{ mg L}^{-1}$ can reach up to 99% or above after 150 hours, while the reaction duration could be shortened to 14 hours and 32 hours respectively with the achievement of the similar degradation rate, when the initial gaseous concentration of $2.0 \times 10^{-3} \text{ mg L}^{-1}$ and $4.0 \times 10^{-3} \text{ mg L}^{-1}$, respectively. The higher the reaction temperature, the shorter the formaldehyde degradation time of diatomite-based nano-TiO₂ photocatalyst required; formaldehyde with an initial concentration of $2.0 \times 10^{-3} \text{ mg L}^{-1}$ was fully degraded at 15 °C for 50 hours, but only took 12 hours at 45°C. Illumination directly drove the formaldehyde degradation capability of diatomite based nano-TiO₂ photocatalyst. When the illumination intensity is 0, formaldehyde was hardly degraded, and only diatomite based nano-TiO₂ photocatalyst was absorbed; under 8100 lx illumination, formaldehyde with a concentration of $2.0 \times 10^{-3} \text{ mg L}^{-1}$ was fully degraded within 14 hours. The higher the ambient relative humidity, the higher the formaldehyde degradation rate of such catalyst; For example, with the relative humidity of 50%, the level of formaldehyde was reduced from $2.0 \times 10^{-3} \text{ mg L}^{-1}$ to $3.72 \times 10^{-5} \text{ mg L}^{-1}$ within 14 hours, while the final formaldehyde concentration can be further reduced to $1.0 \times 10^{-5} \text{ mg L}^{-1}$ when the relative humidity was adjusted to 80%.

To evaluate more porous materials that is used as support for catalyst and figure out the interaction between photocatalyst carriers and photocatalysts, further work are required. And for indoor air purification, much more combo of photocatalyst and photocatalyst carrier need to be tried and finally figure out some effective composite photocatalyst for practical application.

Between them, ACF is much more easier to be access and have good adsorption towards formaldehyde. But in most research, researchers just used pure AC or ACF to be the carrier for the catalyst, few of them focused on the pretreatment of AC or ACF^{9, 35}. In many research pretreating AC or ACF can greatly improve its physical and chemical properties.³⁶⁻³⁸ Due to these studies, my work will aim to combine TiO₂ with functional

ACF.

4. Modification of catalyst

4.1 Doping with metal or nonmetal

Photocatalysis is an emerging and promising technology for the indoor air purification¹⁸, and TiO₂ has been identified as the most effective and useful photocatalyst because of its outstanding physical and chemical properties^{19, 39}. However, with a wide band gap energy of 3.0–3.2eV in TiO₂ that limits the activation of photo-excited electron and holes unless it is irradiated by ultraviolet.⁴⁰ In the enhancement of the photocatalytic efficiency of TiO₂, the modification to TiO₂ by doping with metal or nonmetal has been considered as one of the promising methods⁴¹. Doping with different kind of metal or nonmetal can not only reduce the probability of recombination of electron-hole, but also enhance photo-response of catalyst from ultraviolet to visible range.⁴²

Chen et al.⁴³ indicated that loading Mn-doped TiO₂ on wood-based ACF can improve photocatalytic efficiency and enhance photo-response under visible irradiation. With the increasing of Mn doping concentration and illumination intensity, the degradation rate of HCHO experienced a trend of an increase at first and then decrease afterwards. When the duration of treatment of using 65 W spiral energy saving lamp lighting reached 4 hours, the degradation rate of formaldehyde reached 91% with the initial HCHO concentration of 9.38mg/L, the ingredient of the best performance catalyst was the following: n(Mn):n(Ti)=1:100, and the Mn/TiO₂ to wood-based ACFs dose was 0.22g,

Wang et al.⁴⁴ used inorganic salt TiOSO₄ as the raw material to prepare TiO₂ nano films by using a low-temperature reflow technique on a glass substrate at 130°C. The structural characteristics and photocatalytic degradation of formaldehyde under visible light which were affected by single or double ion doping were then investigated. The results indicated that TiO₂ films, either doped with La³⁺ and Fe³⁺ or co-doped with the same two cations, exhibited the excellent photocatalytic activities in formaldehyde degradation under visible light. Especially for the TiO₂ film that was co-doped with

La³⁺ and Fe³⁺, the degradation rate of formaldehyde reached as high as 90% after a 6-hour visible-light irradiation. The photocatalytic activity of these films under visible light can be ascribed to the nano-scaled anatase structure and the ion-doping, which changes the band gap structures of the TiO₂ material.

Zhang et al.⁴⁵ prepared nano-TiO₂ photocatalyst without doping, with V doping, Ce doping, and V/Ce co-doping by the sol-gel method, and followed by loading on a tile. The prepared catalysts were characterized by XRD and SEM technologies investigate the structure and morphology of samples. The photocatalytic activity of the photocatalyst was evaluated through the formaldehyde degradation. The results showed that the loading capacity of the photocatalyst, the doping amount of the co-doped ions, the doping ratio, and the calcination temperature would affect the photocatalytic activity of nano TiO₂. The V/Ce co-doped TiO₂ photocatalyst was found to have a synergistic effect, and its photocatalytic activity was superior to those TiO₂ without doping and singly-doped TiO₂ samples.

Zhang et al.⁴⁶ used CuCl₂ solution to modify a coconut shell-activated carbon and prepare an activated carbon with a high-capacity formaldehyde adsorption capability. The surface appearance of the AC before and after the modification was characterized by SEM; the impacts of the changes in copper salt concentration on the porous structure of the AC were characterized by nitrogen adsorption-desorption isotherm (N₂/77K); the surface elements and the existence forms of the AC were analyzed with X-ray photoelectron spectroscopy (XPS); the crystalline structure of Cu-carrying activated carbon was studied by XRD; and the formaldehyde adsorption performance of the AC was tested by the dynamic adsorption at ambient temperature. The results showed that, in the modified AC with copper exists in three different forms: Cu, CuCl, and CuCl₂. The number of micro-pores decreased, whereas the proportion of mesopores increased; In addition, with an increase of the concentration of copper salt, the specific surface area and pore volume of AC decreased, while the average pore size increased; the content of oxygen functional groups on the AC surface increased after the modification. When the CuCl₂ concentration was at 0.5 mol/L, the adsorption capacity (4.28mg/g) of modified AC was 3.1 times of that of raw AC without treatment (1.38mg/g). The

obtained formaldehyde adsorption isotherm by the prepared AC agrees well with Freundlich absorption model. .

Yu et al.⁴⁷ prepared N doped TiO₂ powder with Titanium butoxide (TBOT) and urea. The XRD, TEM and UV-vis absorption spectroscopy were used to characterize particle size and properties of phase and absorbance. The results showed that doping with N can effectively inhibit the growth of TiO₂'s crystal grain subsequently decreased the particle sizes of TiO₂. In addition, an appreciable enhancement of absorption effect was observed by doping with N. The Density Function Theory (DFT) was used and found the decreased band gap due to the doping of nitrogen. Furthermore, the redshift of absorption spectrum of TiO₂ by doping with N was also found to contribute. The research also indicated that interstitial N-doped TiO₂ is more beneficial to the light absorption compared with the substitutional N-doped TiO₂.

4.2 Modifying with noble metals

Supported noble metal catalysts are prepared by modifying catalysts with noble metals. Different from the photocatalytic effect of TiO₂ against formaldehyde, the catalytic principle of supported noble metal catalysts is known as thermal catalytic oxidation, and the mechanism is described as follows. At a certain temperature and with the presence of oxygen, oxygen molecules will be dissociated into oxygen atoms, charged peroxide and superoxide radicals when they adsorb on the surface of transition metals or some noble metals, and these activated oxygen will easily react with the harmful gases in the air and produce degraded substances such as CO₂ and H₂O.

Shi Y., et al.⁴⁸ used CeO₂ as a supporter to prepare a supported Pt catalyst by impregnation method for a low-temperature formaldehyde oxidation. The influence of Pt precursor and Pt loading on the catalytic performance were investigated. The results showed that the catalyst using Pt(NO₃)₂ as the precursor has higher catalytic activity than that was prepared with H₂PtCl₆ as the precursor during formaldehyde degradation. This difference lies in the presence of Cl⁻ weakening catalytic activity of the catalyst. In addition, the activity of the catalyst would increase with an increase of

Pt loading. The conversion ratio of formaldehyde at 30 °C was above 80% when the Pt loading was 3%.

Tana⁴⁹ loaded two supportors (Fe₂O₃ and NiO) with Au by using co-precipitation method and deposition-precipitation method respectively to prepare different quasi-catalysts, and then calcined the quasi-catalysts at different temperatures to obtain the final catalysts. Results about the catalytic oxidation activity of the catalysts against formaldehyde showed that formaldehyde was found on the Au/Fe₂O₃ catalysts, and catalytic activity of the catalysts decreased with an increase of calcination temperature. For the Au/Fe₂O₃ catalysts, the Au nanoparticles prepared by deposition precipitation method were smaller than those prepared by co-precipitation method, which explains why catalysts prepared by deposition precipitation method have higher activity in catalytic oxidation of formaldehyde.

Chen et al.²⁹ loaded nest-like MnO₂ with both Pt and Au to prepare Au_{1-x}Pt_x/MnO₂ catalysts. They found that catalytic activity of the catalysts is greatly influenced by the Au/Pt ratio, and state of Au and Pt, whether they are in the ionic state. Au-Pt alloy particles would bring better catalytic performance than Au-Pt nanoparticle mixtures, and the Au_{0.5}Pt_{0.5}/MnO₂ catalyst has the best catalytic performance and a fully decomposition of formaldehyde at 40 °C can achieve.

Zhang et al.⁵⁰ loaded TiO₂ with Pt, Rh, Pd, and Au respectively to prepare catalytic degradation agents against formaldehyde, and investigated their catalytic activity at room temperature. They found that the order of activity of the four catalysts in catalytic oxidation of formaldehyde to formate species was Pt/TiO₂ > Rh/TiO₂ >> Pd/TiO₂ > Au/TiO₂. In the subsequent experiment, it was found that formate could be decomposed to the adsorbed CO species followed by the oxidation to CO₂ on the Pt/TiO₂ catalyst. By contrast, formate was less likely to be decomposed to the adsorbed CO species on the Rh/TiO₂ catalyst. Therefore, among the four noble metals, only the supported Pt catalyst can realize complete removal of formaldehyde through catalytic oxidation at room temperature.

5. Synthesis methods

A series of methods such as sol-gel, precipitation, co-precipitation, impregnation hydrothermal and template can be used for synthesis of photocatalysts for formaldehyde degradation. To strengthen photocatalysts performance and their catalytic activities, many researches that put emphasis on enhancing and modifying photocatalysts preparation methods have been published recently. It can be believed that improving synthesis methods and optimizing reaction conditions can enhance photocatalysts properties and modifying their structures.

Luo et al.⁵¹ prepared nano titanium dioxide powder by using the special liquid precipitation method. The impregnation method was used to obtain AC-supported nano-titanium dioxide to integrate the catalytic performance of TiO₂ and the dispersing performance of AC. The degradation rate of the simulated wastewater (acidic fuchsin solution) —by the catalyst under natural light was explored. The impacts of different composite proportion and catalyst volume on the photocatalytic efficiency and catalyst recycling were discussed. The results showed that the most optimum catalytic effect was achieved when the mass ratio of the titanium dioxide to AC was 2:1; the optimal catalytic effect was achieved with the following conditions 160 mL of acidic fuchsin solution with a mass concentration of 10 mg/L with addition of 1 g of the catalyst. The degradation rate reached 98% after 50 minutes. The recycled catalyst showed similar performances of 97% (50 mins) which was approximately equivalent to the first degradation rate.

Liu et al.⁴ prepared TiO₂ aero-gel with a mesh-like structure and nanometer grain size by the Sol-Gel method together with supercritical drying method, while activated carbon fiber (ACF) was used as a carrier. TiO₂ was loaded on the ACF through the impregnation method, whereas TiO₂/ACF composite materials with high photocatalytic activity and strong absorption were obtained through a vacuum calcination at 450°C; The organic pollutants in the air and degraded by ultraviolet light. Sol-gel was prepared by taking tetrabutyl orthotitanate (Ti (OC₄H₉)₄) as the raw materials, and taking ethyl alcohol, acetic acid and acetone as hydrolysts; the mixture ratio of the sol reagents were

20 : 40 : 4.4-5 : 0.18 : 1.5-2 (volume ratio) for $\text{Ti}(\text{OR})_4$: EtOH : H_2O : CH_3COOH : ACACH (acetylacetone). It was observed by SEM that: 1) Alcolgel possesses a mesh-like structure; 2) The evenly loaded TiO_2 on each fiber of the ACF and even particle sizes ranging between 40~50 nm were observed by different characterization techniques. Using formaldehyde as the target pollutant, a quick decrease of the concentration of the free formaldehyde from 6.58 mg m^{-3} to 0.99 mg m^{-3} within 25 minutes was observed, and the formaldehyde removal performance of the composite TiO_2 /ACF being subjected to supercritical drying was found to be superior to that the catalyst prepared by conventional drying approach.

Huang et al.⁵² prepared nano crystalline anatase titania powders by mixing solution of $\text{Ti}(\text{SO}_4)_2$ (0.5M) and urea via hydrothermal treatment . The crystal phase, grain size and morphology of the prepared powders were studied by the influences of $[\text{Ti}(\text{SO}_4)_2]/[\text{Urea}]$, temperature and soaking time were discussed in details. The prepared TiO_2 powders are anatase with 10-20nm in diameter under the conditions of the ratio $[\text{Ti}(\text{SO}_4)_2]/[\text{Urea}] = 1:2-1:4$ and $140-200^\circ\text{C}$ for 2-6 hours. The experiment shows that the grain size increases with the decrease of the molar ratio $[\text{Ti}(\text{SO}_4)_2]/[\text{Urea}]$, rise in reaction temperature and prolongation of soaking time.

6. Conclusion

Loading TiO_2 on porous materials such as activated carbon fiber (ACF) and attapulgite has recently being the focus of many researches²⁹. Because of its high stability, high recycle rate, mechanical resistance, optimum porosity and high surface area, ACF is widely used as commercial adsorbent and support for different type of catalyst. Also, pretreated ACF will have better physical and chemical properties.³⁸ In order to narrow the energy band gap, the metallic or non-metallic doping of TiO_2 is the general employed approach. Because of its similar atomic radius to Ti^{4+} , the Iron (Fe^{3+}) is considered to be an ideal metal to be doped in TiO_2 .⁴¹ Doping TiO_2 with non-metallic anions, such as N, S, and C, have been found to be a promising strategy for extending the optical spectrum of TiO_2 from the UV to the visible light regions⁵³⁻⁵⁴. And among

them, TiO₂ doped with N can be a good alternative as it can effectively narrow the band gap, inhibit the growth of crystal grain of TiO₂ and allow the photocatalytic degradation of formaldehyde under visible light irradiation ⁵⁵.

In this work, the degradation of formaldehyde using Fe, N-codoped-TiO₂ loaded on modified ACF photocatalyst under visible irradiation is reported. Because of its simplicity and cost-effectiveness in preparing the catalyst, the reported process in this work shows a rosy prospect in the industrial application..

The research methodology are summarized below.

1. The design of static chamber for photo-catalytic reaction/degradation of formaldehyde
A sealed glove box fitted with a UV light and ordinary light was designed to simulate an indoor environment.
2. The modification of activated carbon fiber (ACF)
To find the best treatment method for ACF, different reagents were used to modify ACF.
3. The synthesis of Fe, N-co-doped TiO₂/ACF
 - i. The photocatalyst was synthesized using a modified sol-gel method .
 - ii. To figure out the most suitable doping ratio, different dosage of N and Fe will be used.
 - iii. Subjected to the high temperature, Fe, N-codoped TiO₂ will be loaded on the modified ACF and the Fe, N-codoped TiO₂/ACF will be synthesized.
4. Photocatalytic tests: Synthesized photocatalysts were tested and compared for their formaldehyde degradation efficiency, under similar conditions.

This work focused on improving the reaction condition of the synthesis of Fe-N-TiO₂/ACF, the degradation rate of formaldehyde under visible light and the characterization of the produced catalysts. The characterization of the prepared photocatalyst were: X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and Brunauer–Emmett–Teller analysis (BET).

Chapter 2. Experimental

2.1. Preparation of Photocatalyst

2.1.1 Surface functionalization of ACF

One gram of Activated carbon fibre (ACF) (specific surface area: 1800-2000 m²/g, model: KJF1800-2000) (Kejing Carbon Fiber CO., LTD, Jiangsu) was soaked in different solutions including 1mol/L sodium hydroxide (NaOH, AR, Sinopharm Chemical Reagent CO., LTD, Shanghai) and 0.5, 0.75, 1.00, 1.25, 1.5, 1.75, 2.00, 2.25 mol/L nitric acid (HNO₃, AR, Sinopharm Chemical Reagent CO., LTD, Shanghai) for 1 hour. After soaking, the treated ACF was washed with distilled water 3 times. Then, the washed ACF was dried at 120 °C for 12 hours and stored for further application.

2.1.2 Surfactant-assisted synthesis of TiO₂ sol with co-doping of Fe and N

Seven milliliters of tetrabutyl orthotitanate (TBOT, CP, Sinopharm Chemical Reagent CO., LTD, Shanghai) and different volume of sodium dodecyl benzene sulfonate (SDBS, AR, Sinopharm Chemical Reagent CO., LTD, Shanghai) were added in anhydrous alcohol in the ratio of 1:4 (volume ratio) and the resulting solution was stirred for 1 hour and named solution A.

Solution B was prepared by mixing 16 mL of glacial acetic acid (GR, Sinopharm Chemical Reagent CO., LTD, Shanghai) and different volumes of 6 mL, 9 mL, 12 mL, 15 mL and 18 mL deionized water in 25 mL of absolute alcohol (GR, Sinopharm Chemical Reagent CO., LTD, Shanghai). To prepare Fe-N-codoped TiO₂, 0.072 g Iron (III) nitrate nonahydrate (AR, Sinopharm Chemical Reagent CO., LTD, Shanghai) and 0.858 g urea (AR, Sinopharm Chemical Reagent CO., LTD, Shanghai) were mixed with solution B, the dosage of Fe and N were 0.01 and 0.4 in mol basis, respectively. And then the solution A was added dropwise under continuous stirring for 1 hour.

2.1.3 Fe, N co-doped TiO₂ loaded on functionalized ACF

One gram of pretreated ACF was then added into TiO₂ sol and the mixture was placed in an oven at 110 °C for 12 hours. The resulted samples were then subjected to heat treatment in a calcination oven under nitrogen atmosphere at different temperatures (350 °C, 375 °C, 400 °C, 425 °C, 450 °C) for 2 hours. The final sample was designated as 0.4N-0.01Fe-TiO₂/ACF.

2.2 Preparation of Control Group

As control group of the experiment, ACF without functionalization, TiO₂ without doping and photocatalyst with TiO₂ loaded on ACF were prepared.

2.2.1 Preparation of ACF with none functionalization

ACF was soaked in distilled water for 1 hour. After soaking, ACF was washed with distilled water for 3 times. Then, the washed ACF was dried at 120 °C for 12 hours and stored for further application.

2.2.2 Preparation of TiO₂ without doping

Seven milliliters of TBOT was added in anhydrous alcohol in proportion of 1:4 (volume ratio) and the resulted solution was stirred for 1 hour and named solution A.

Solution B was prepared by mixing 16 mL of glacial acetic acid and 12 mL distilled water in 25 mL of absolute alcohol. And then solution A was added into solution B dropwise under continuous stirring for 1 hour.

2.2.3 Undoped-TiO₂ loaded on ACF with none functionalization

Pretreated ACF was then added into TiO₂ sol and the mixture was placed in an oven at 110 °C for 12 hours. The resulted samples were subjected to heat treatment in a calcination oven under nitrogen atmosphere at 400 °C for 2 hours and finally undoped-TiO₂/ACF samples was obtained and it would be named as undoped in Chapter 3 as the

control group to compared with other sample.

2.3. Experimental setup

Formaldehyde-enriched indoor air environment was simulated within a cube reactor made of polymethyl methacrylate (PMMA) with an internal volume of 125 L (0.125 m^3) and fitted with a pair of corrosion resistance gloves, evaporation fan and fluorescent tube of 32 W , as shown in Fig 1 below.

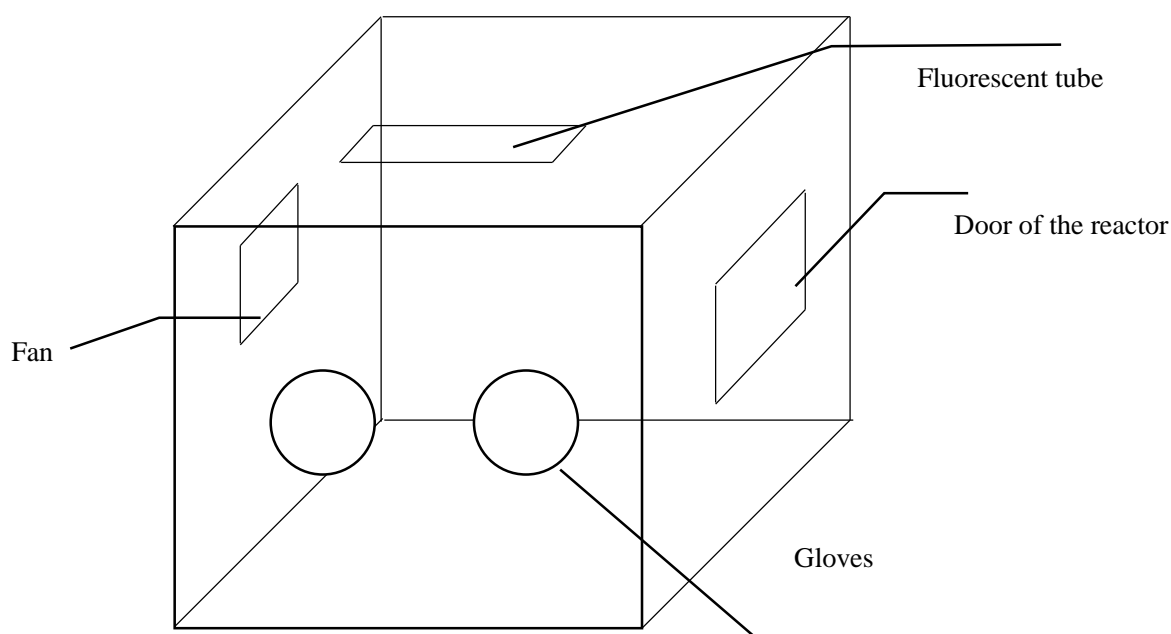
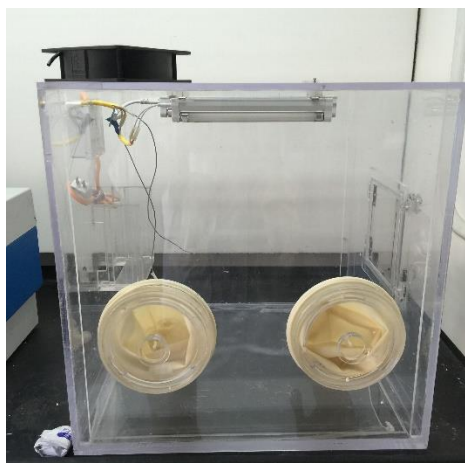


Fig. 1. Photo and diagram of the photocatalytic reactor

Firstly, an evaporating dish containing a certain mass of photocatalyst sample was covered with aluminium-foil paper which was used to isolate the photocatalyst from

formaldehyde and placed in the reactor. At the same time, an evaporating dish containing 2.5 mL standard solution of formaldehyde which was prepared by adding 2.8 mL 37% formaldehyde (Sinopharm Chemical Reagent CO., Ltd, Shanghai), solution into a 1L volumetric flask and diluting with distilled water, was placed in the reactor for 0.5 hour. With flow of the air initiated by the fan, the solution was effectively evaporated as gaseous formaldehyde. A formaldemeter (PPM-HTV PPM Technology Ltd., England) which can measure the concentration of formaldehyde from 0 to 20 ppm was used to measure the concentration of formaldehyde in the chamber. After the concentration of formaldehyde had stabilized at approximately 20 ppm, the catalysts was uncovered by removing the aluminium-foil paper and the evaporating dish containing the standard solution of formaldehyde was covered with the foil paper, with the help of the gloves. The photocatalytic performance of 0.4N-0.01Fe-TiO₂/ACF photocatalyst was investigated, and its ability to degrade HCHO gas under visible irradiation was measured by introducing a degradation efficiency parameter.

2.4. Removal efficiency of photocatalyst

Based on the experimental method highlighted above for the synthesis of N-Fe-ACF/TiO₂, certain synthesis parameters were varied to optimize the produced photocatalyst. The parameters include: volume of hydrolysis water in solution B, calcination temperature, different pretreatment solutions for ACF, concentration of nitric acid to pretreat ACF, the volume of sodium dodecyl benzene sulfonate (SDBS). Studies on the degradation rate of formaldehyde were conducted in a 50 cm*50 cm*50 cm polymethyl methacrylate operation box with visible light irradiation. And thus, the influence of water consumption, calcination temperature, different pretreated activated carbon fibers and surfactant concentration on the degradation efficiency of mixed materials catalysts, were determined.

Photocatalytic efficiency of the prepared catalysts were measured by removal efficiency of the formaldehyde gas. In a typical test, photocatalyst that had been tailored as 1g being added into the reaction chamber, which was filled with formaldehyde gas

(20ppm). The photocatalyst was then irradiated under visible light to degrade gaseous formaldehyde. The removal efficiency of the photocatalyst was calculated as follows:

$$\eta = \frac{C_0 - C_t}{C_0} \times 100\%$$

Where C_0 is the initial concentration of formaldehyde, C_t is residual concentration of formaldehyde at time of t .

2.5. Characterization techniques

The samples of undoped-TiO₂ and Fe-N-TiO₂ were measured by XRD on a powder crystal X-ray diffractometer (Ultima IV, Japan). The surface micromorphologies of photocatalysts and energy dispersive spectra of the 0.4N-0.01Fe-codoped TiO₂ powders were characterized and recorded on through SEM (JSM7401F, Japan) at an accelerating voltage of 10.0 kV, respectively. Specific surface area of the samples of TiO₂/ACF and Fe-N-TiO₂/ACF (SBET, m² · g⁻¹) were calculated by BET method (V-Sorb 2800P, Gold APP Instruments).

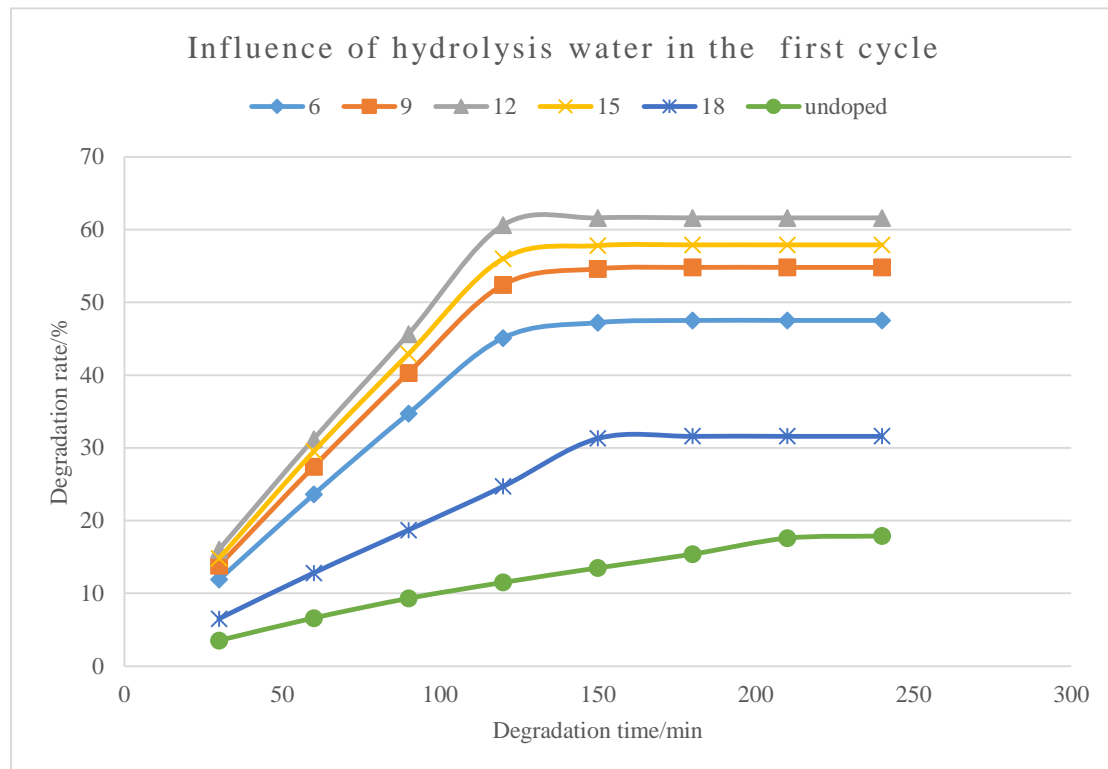
Chapter 3. Results and Discussion

3.1 Dependence of Photocatalytic Performance on the Synthesis Factors of Fe, N co-doped TiO₂ Supported Functionalized ACF

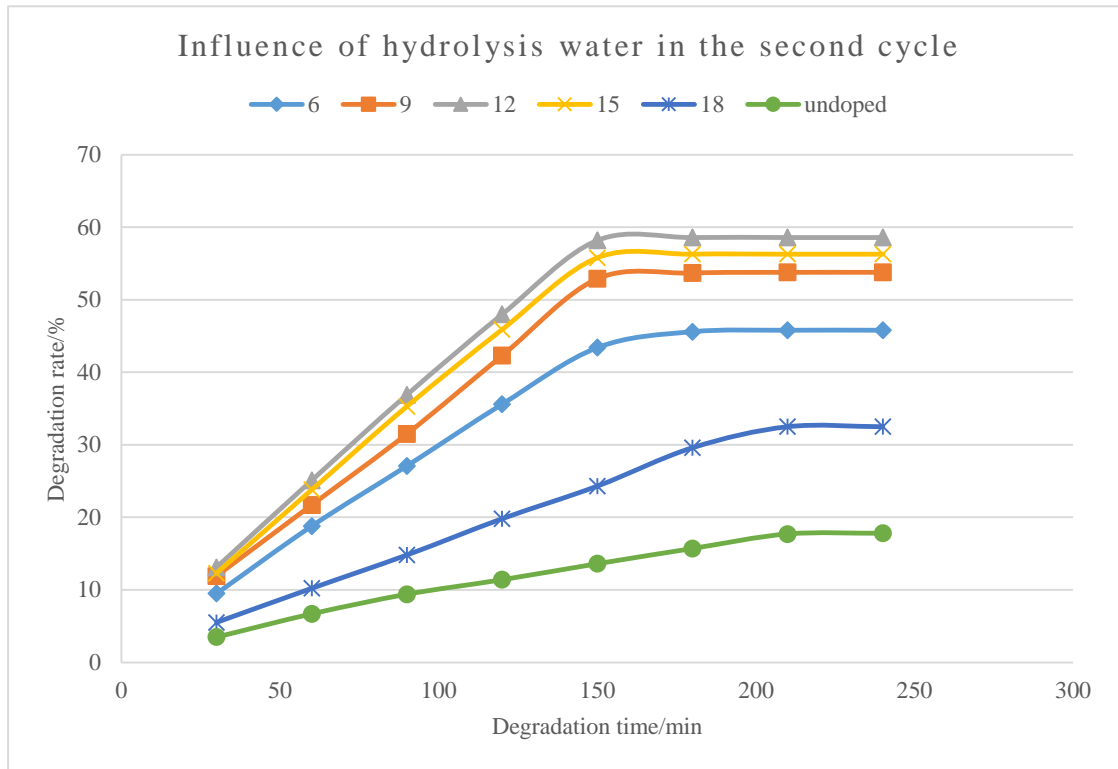
3.1.1 Influence of hydrolysis water

In this study, the influence of hydrolysis water on the degradation efficiency of the generated catalysts was evaluated. The photocatalyst was prepared by ACF with addition of 1.5 mol/L HNO₃, Solution A without surfactant and calcination temperature with 400 °C. When the amount of TBOT in solution A is 7 mL and the amount of deionized water in solution B were 6 mL, 9 mL, 12 mL, 15 mL and 18 mL, respectively. As control group, degradation efficiency of photocatalyst that prepared by undoped TiO₂ loaded on ACF without functionalization was added in the graph. The degradation

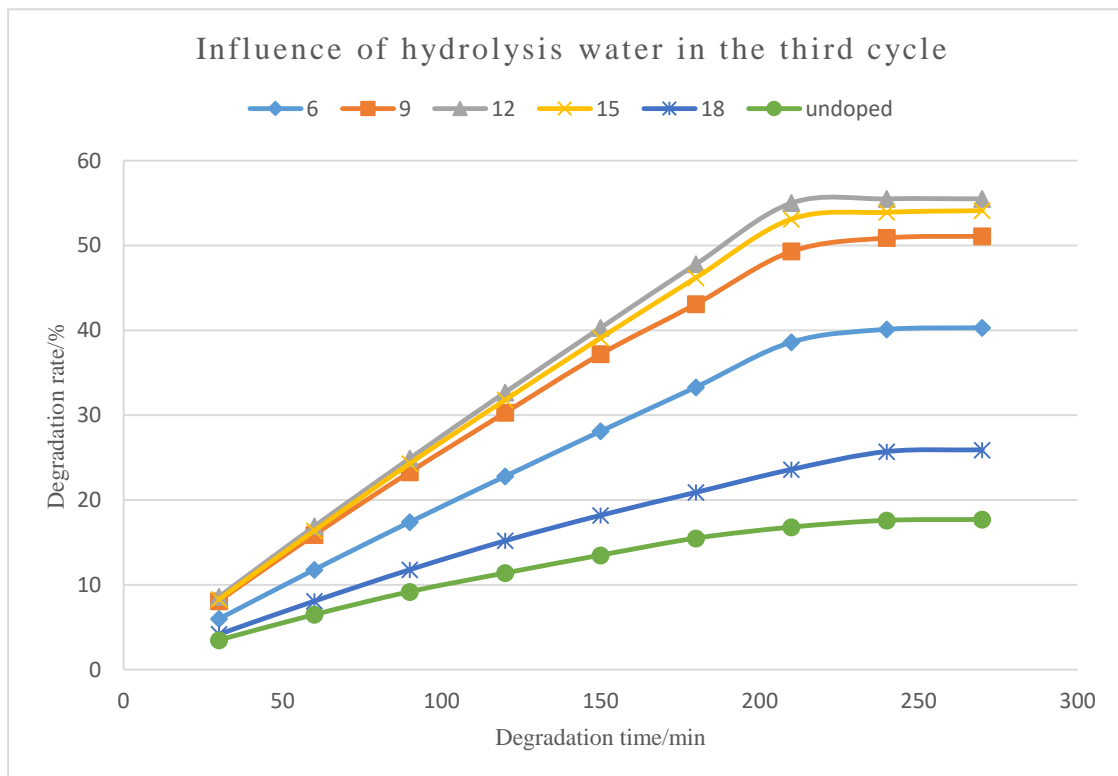
efficiency of formaldehyde by photocatalyst at room temperature as a function of the amount of hydrolysis water is presented in Figure 2. As control group, degradation efficiency of photocatalyst that prepared by undoped TiO_2 loaded on ACF without functionalization was added in the graph and named as undoped. The experiment was conducted under the irradiation of fluorescent tube.



(a)



(b)



(c)

Fig.2 (a), (b), (c) different volume of hydrolysis water on degradation rate of formaldehyde of N-Fe-TiO₂/ACF (0.4N-0.01Fe-TiO₂/ACF?) after three cycles

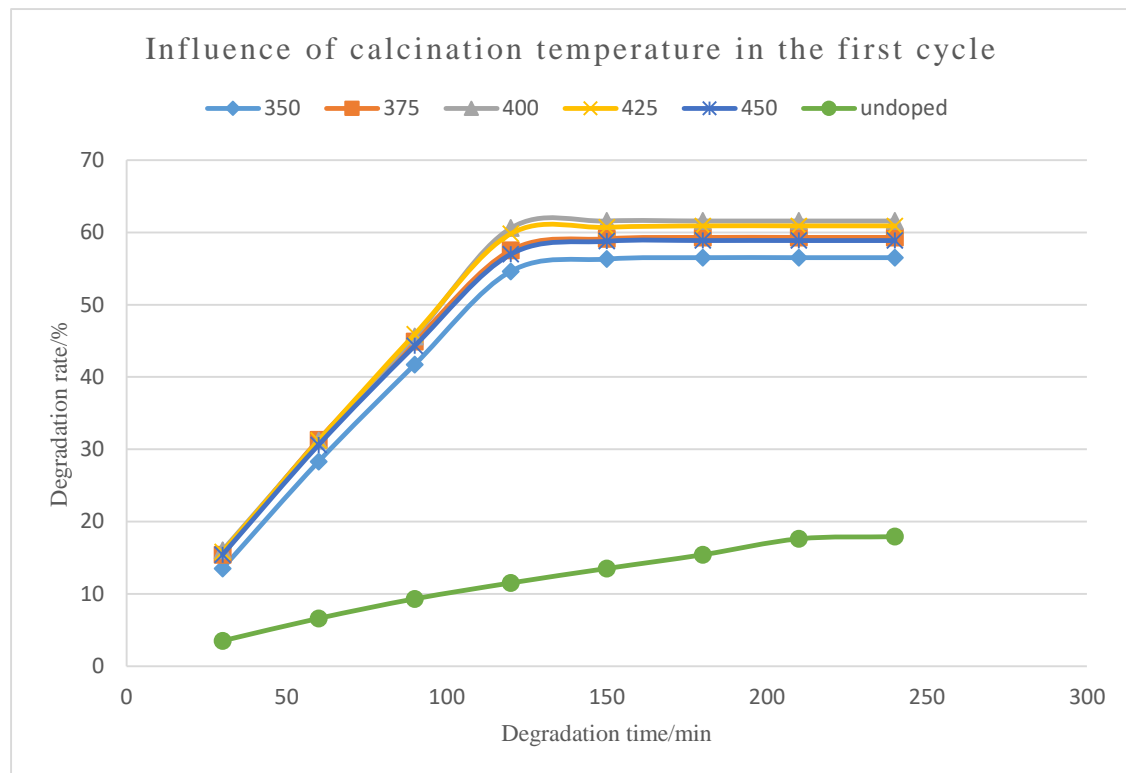
It can be seen from Fig. 2 that the degradation efficiency of formaldehyde increases with an increase of the amount of hydrolysis water; when the amount of water reaches 12ml (the volume ratio of water and TBOT is 12: 7), the degradation efficiency peaked at the degradation rate of 61.6 %, 58.6 % and 55.5 % in the first, second use and the third cycles, respectively. Then degradation efficiency decreased with an increase of hydrolysis water. In addition, a slight decrease of removal efficiency of photocatalyst was observed as cycle proceeded.

According to research findings,⁵⁶ when the hydrolysis water is little, the solvent predominates in the system; the probability of TBOT contacting with water decreases with slow hydrolytic speed. Meanwhile, excess titanium alkoxide in the solution tends to form Ti-O-Ti chains through the alcohol-oxygen bridge. Each Ti is connected with 4 O atoms, ultimately forming a three-dimensional network structure. And the product is easy to aggregate, prolonging the gel time. Increasing the amount of hydrolysis water results in obviously shortening the duration of gel formation. As water consumption increased, the $Ti(OH)_4$ tended to present the higher hydrolysis rate, which led to the weakening of the bonding bridge between the alcohol and oxygen. Furthermore, excess water inhibits Ti-O-Ti formed by butoxy alkoxide through oxolation and generates a large amount of Ti-OH that results in sol ions becoming loosing and unable to form a three-dimensional network structure.⁵⁶ According to experiments, it shows that the photocatalytic efficiency of the product is optimal when the volume ratio of water (12 mL) and tetrabutyl titanate (7 mL) is 12: 7. Therefore, the optimal volume ratio of water in Solution B and tetrabutyl titanate in Solution A was chosen at 12: 7.

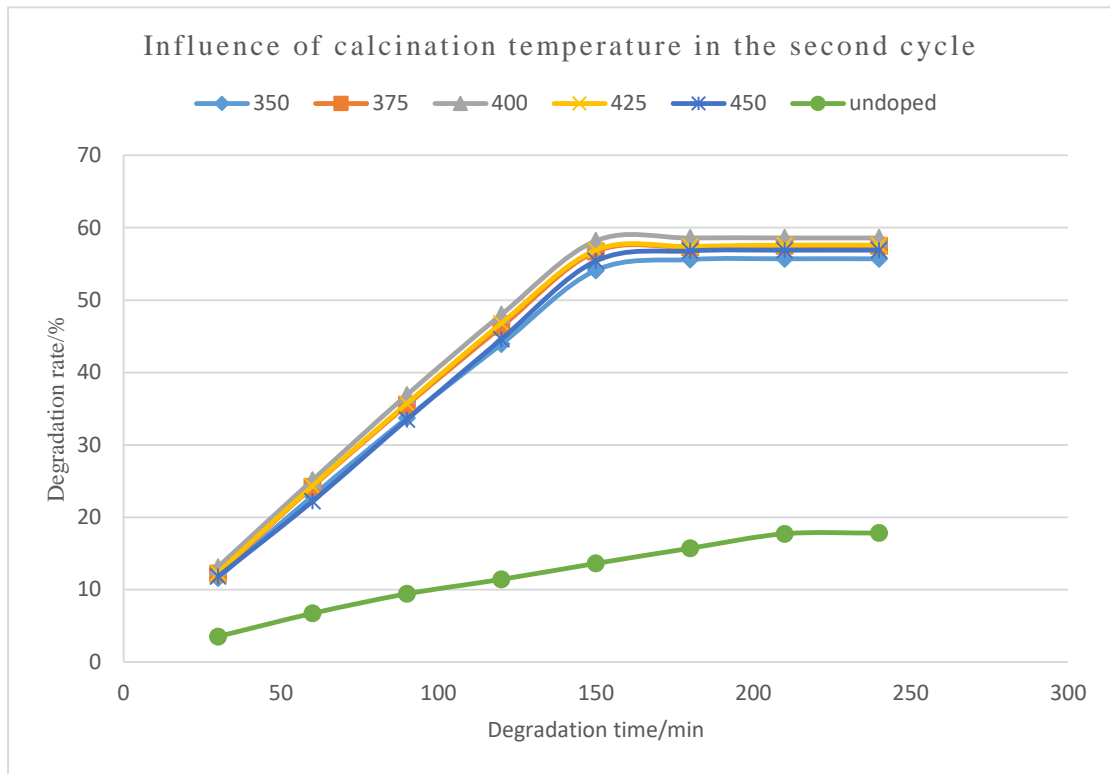
3.1.2 Influence of calcination temperature

In this study, the influence of calcination temperature on the degradation efficiency of N-Fe-ACF/ TiO_2 was investigated. The photocatalyst was prepared by ACF with 1.5 mol/L HNO_3 , Solution A without surfactant and ratio of 12 to 7 between water and TBOT in solution B. When the calcination temperature of the muffle furnace is set at, The degradation efficiency of formaldehyde by different catalyst calcined at 350 °C,

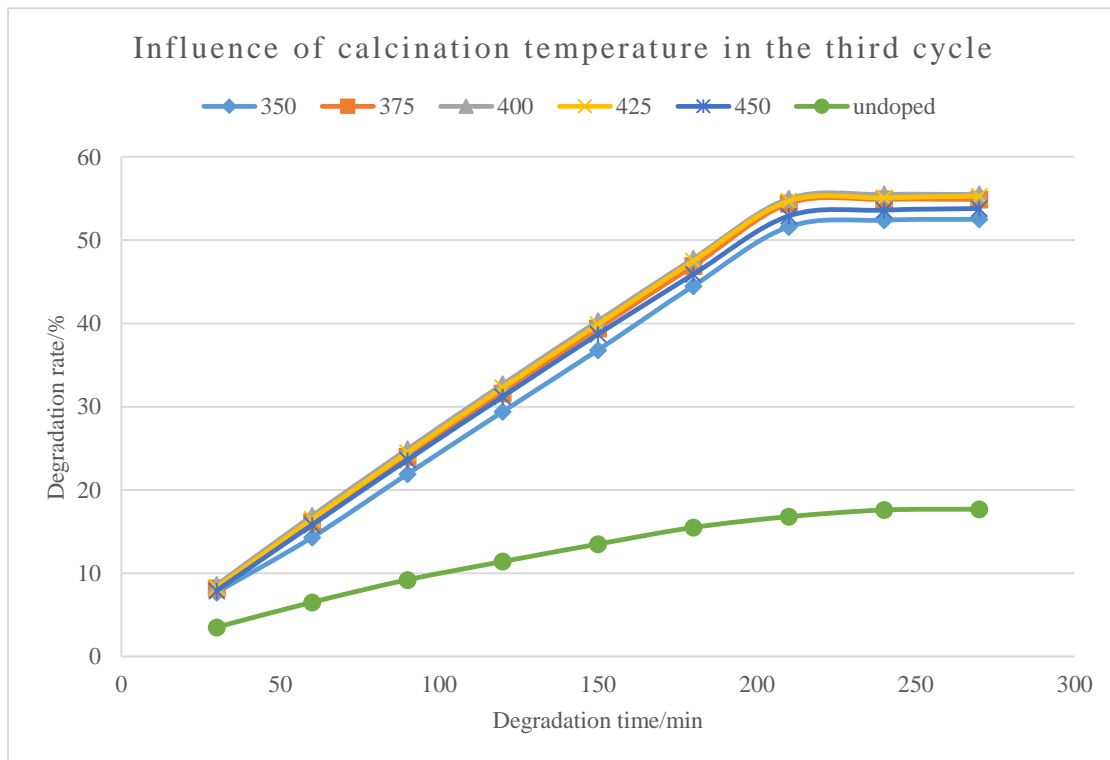
375 °C, 400 °C, 425 °C and 450 °C is presented in Fig.3. As a control, degradation efficiency of photocatalyst that prepared by undoped TiO₂ loaded on ACF without functionalization was added in the graph and named as undoped. The experiment was conducted under the irradiation of fluorescent tube.



(a)



(b)



(c)

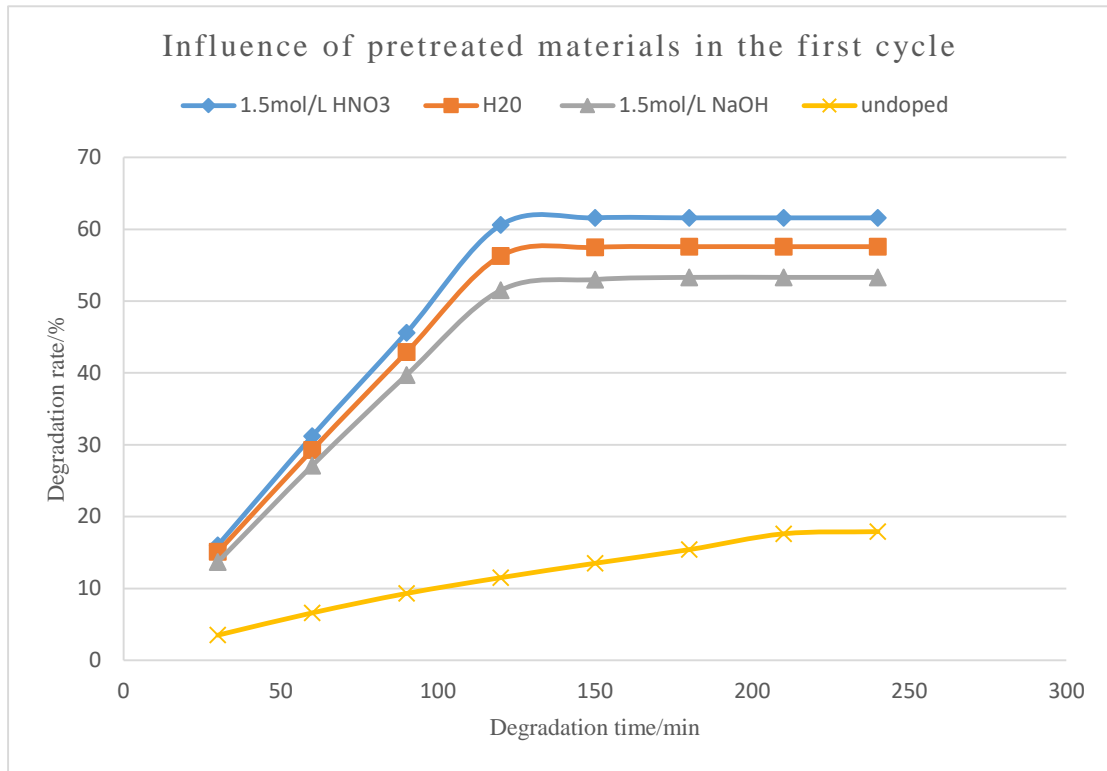
Fig. 3 (a), (b), (c) The influence of the calcination temperature of the muffle furnace on the degradation efficiency in three cycles

According to Fig. 3, it can be seen that the degradation efficiency of formaldehyde will increase continuously as the calcination treatment temperature rises. The 400 °C was found to be optimal calcination temperature with the degradation efficiency of formaldehyde reaching 61.6 %, 58.6 % and 55.5 %, respectively during the first, second and the third use of catalyst. As the reuse continued, degradation rate of the photocatalysts dropped accordingly.

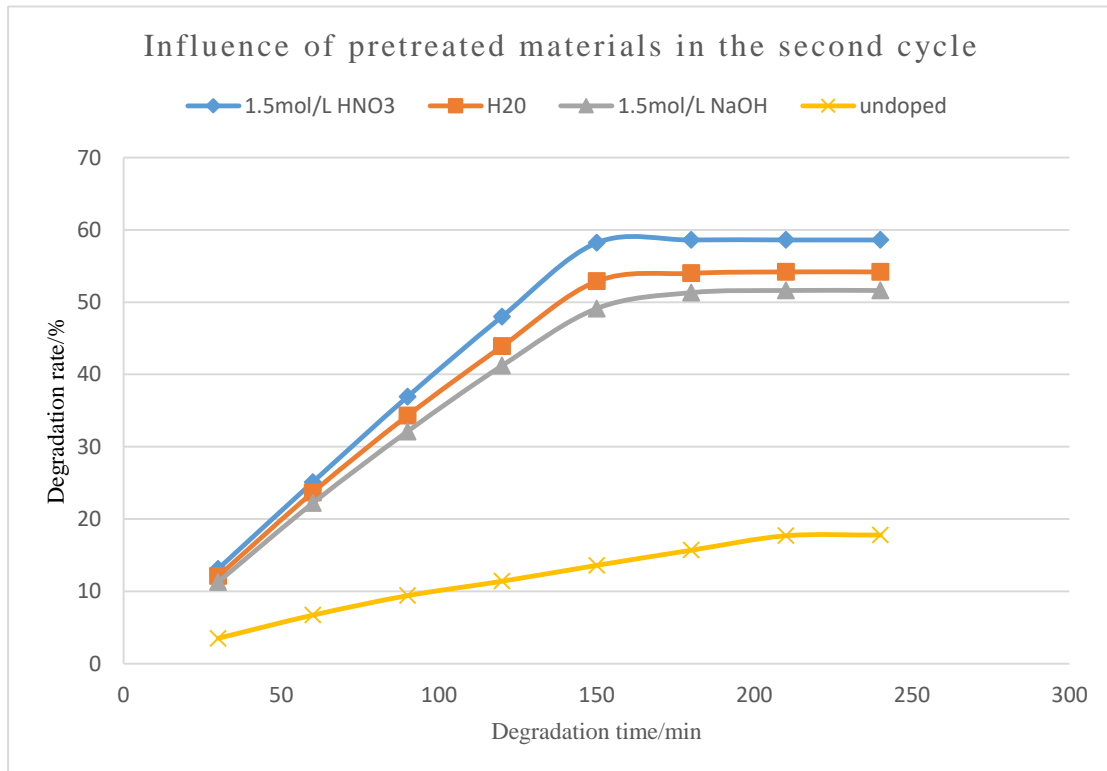
According to research findings⁵⁷, the crystal forming of the photocatalyst can be determined by the calcination temperature. The photocatalyst mainly exists in the form of anatase when the calcination temperature is low. Also, the photocatalyst changes from an amorphous state to an anatase or even rutile ore with high activity of catalyst along with the rise of calcination temperature. But the too higher temperature might lead to adverse effect leading to the decrease of activity due to inhabitation of the crystal formation and enlarging aperture of photocatalyst⁵⁷. The experimental results showed that the photocatalysts calcined at 400 °C exhibited the best photocatalytic performance compared to other temperatures.. Therefore, the calcination temperature was maintained at 400 °C in further experiments.

3.1.3 Influence of Activated Carbon Fibers pretreatment/functionalization methods

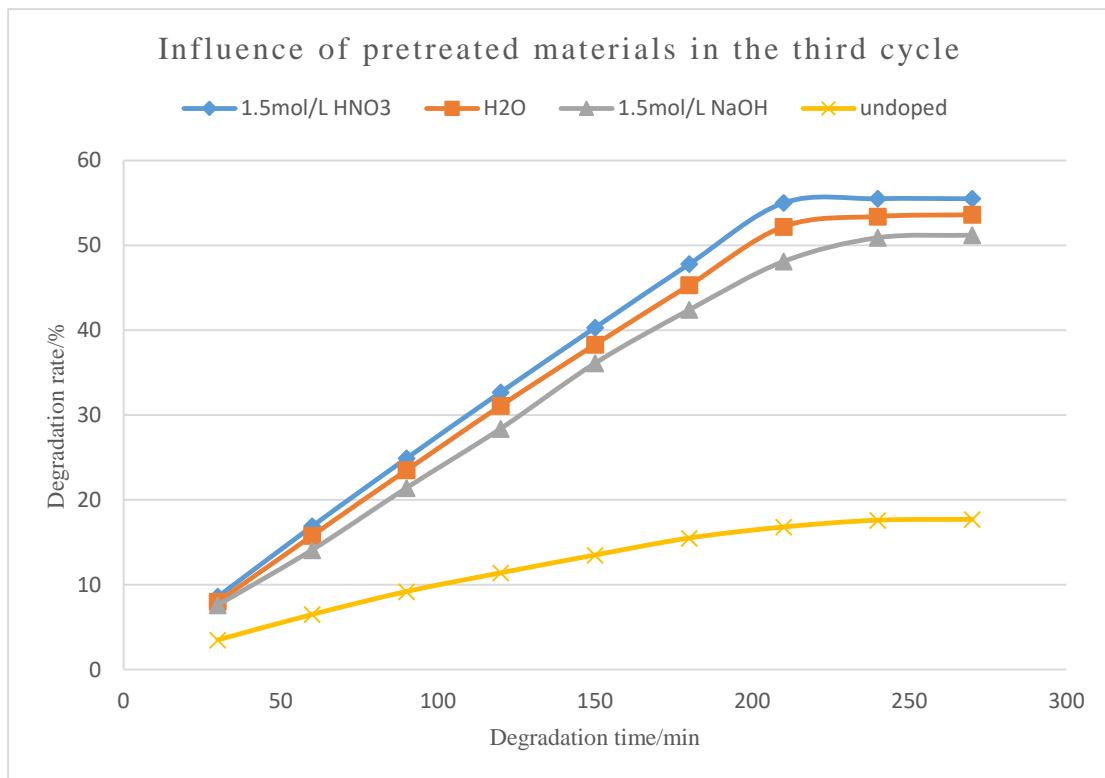
In this section, the influence of different pretreatment conditions of ACF on the degradation efficiency of the catalyst were examined. The photocatalyst was prepared by Solution A without surfactant, with the ratio of 12 to 7 between water and TBOT in solution B and calcined at 400 °C. According to some researches, different solvents such as HNO₃, H₂O and NaOH can be adopted to pretreat ACF, respectively^{38, 58}. In this way, the influence of different pretreated materials on the degradation efficiency of the catalyst of mixed materials are shown in Fig. 4. As control group, degradation efficiency of photocatalyst that prepared by undoped TiO₂ loaded on ACF without functionalization was added in the graph and named as undoped. The experiment was carried out under the irradiation of fluorescent tube.



(a)



(b)



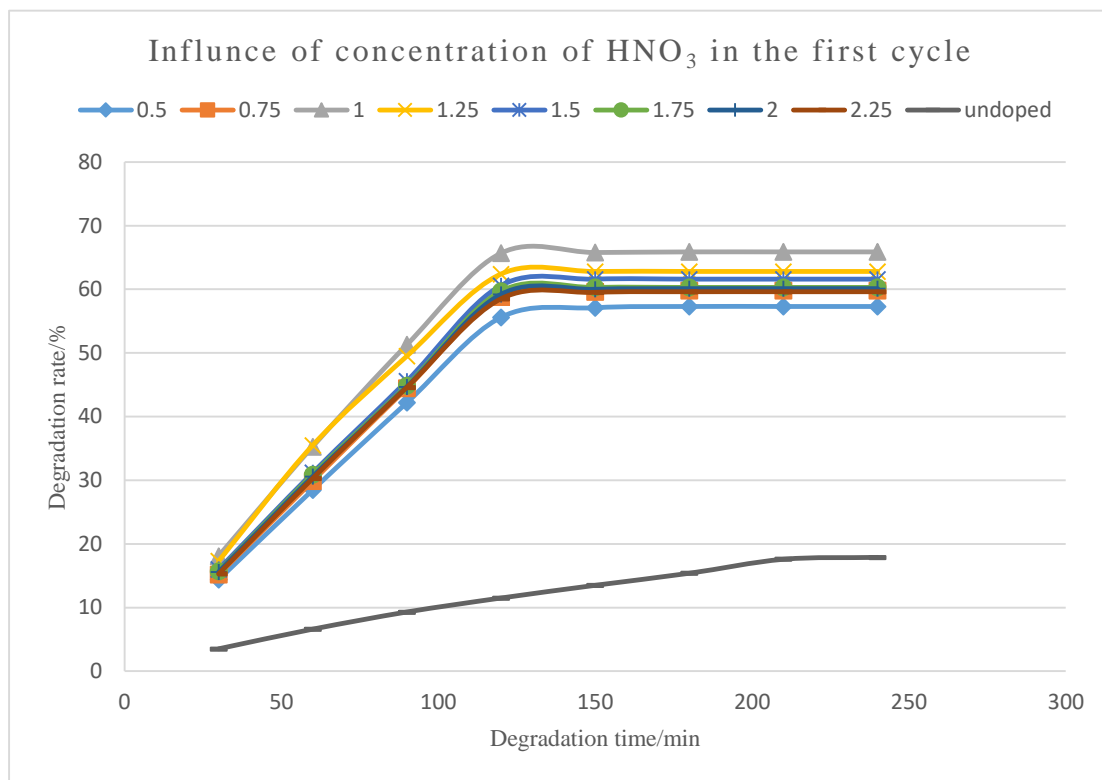
(c)

Fig. 4(a), (b), (c) The influence of pretreated materials of different activated carbon fiber on the degradation efficiency in three cycles

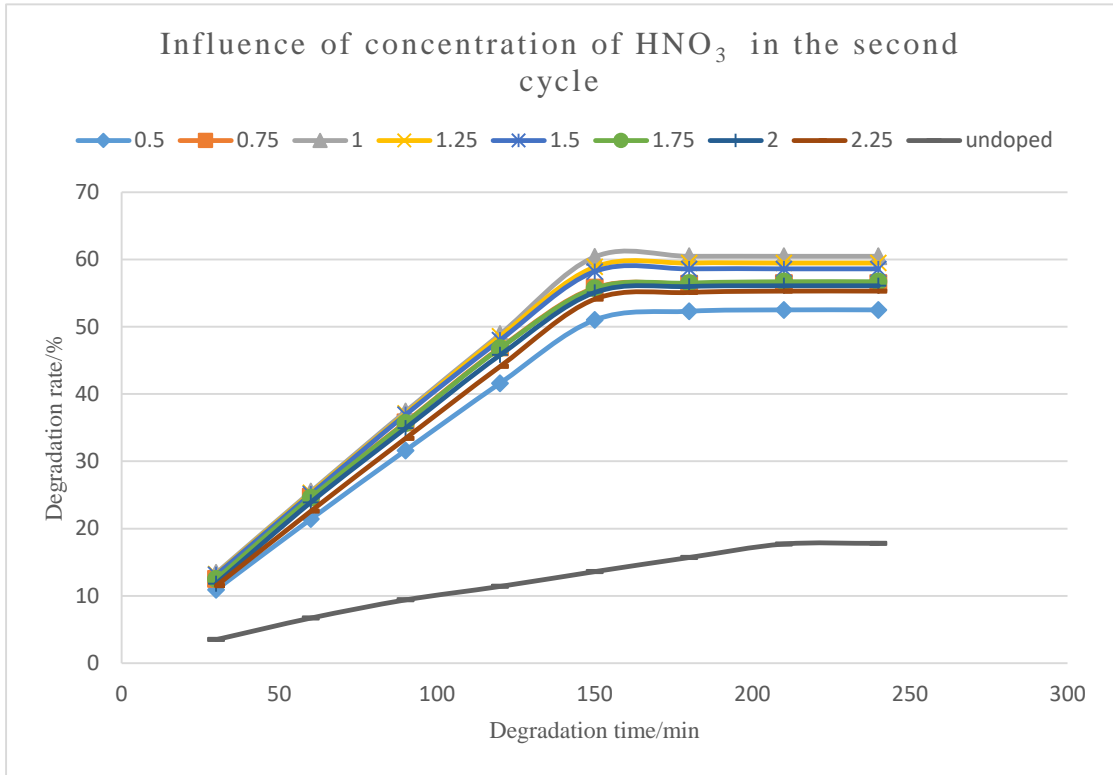
It can be seen from Fig. 5 that the degradation efficiency of formaldehyde by ACF pretreated by HNO₃ is significantly higher than that being pretreated by NaOH and H₂O. This is because the increased number of oxygen-containing functional groups on the surface of the sample modified by HNO₃ contributes to the obviously-increasing proportion of functional groups such as C=O and O—C=O on the surface of activated carbon, the existence of these functional groups are found to be favorable for the adsorption of formaldehyde gas.³⁸ The reason that sample modified by NaOH possessed lower degradation rate of formaldehyde is because modified by NaOH will decrease the number of oxygen-containing functional groups on the sample surface.⁵⁹ Above all, the experiment was conducted by using HNO₃ degradation efficiency in the further research of the project.

Furthermore, the influence of concentration of HNO₃ on the degradation efficiency of the catalyst was studied. The photocatalyst was prepared by Solution A without surfactant, ratio of 12 to 7 between water and TBOT in solution B and calcination

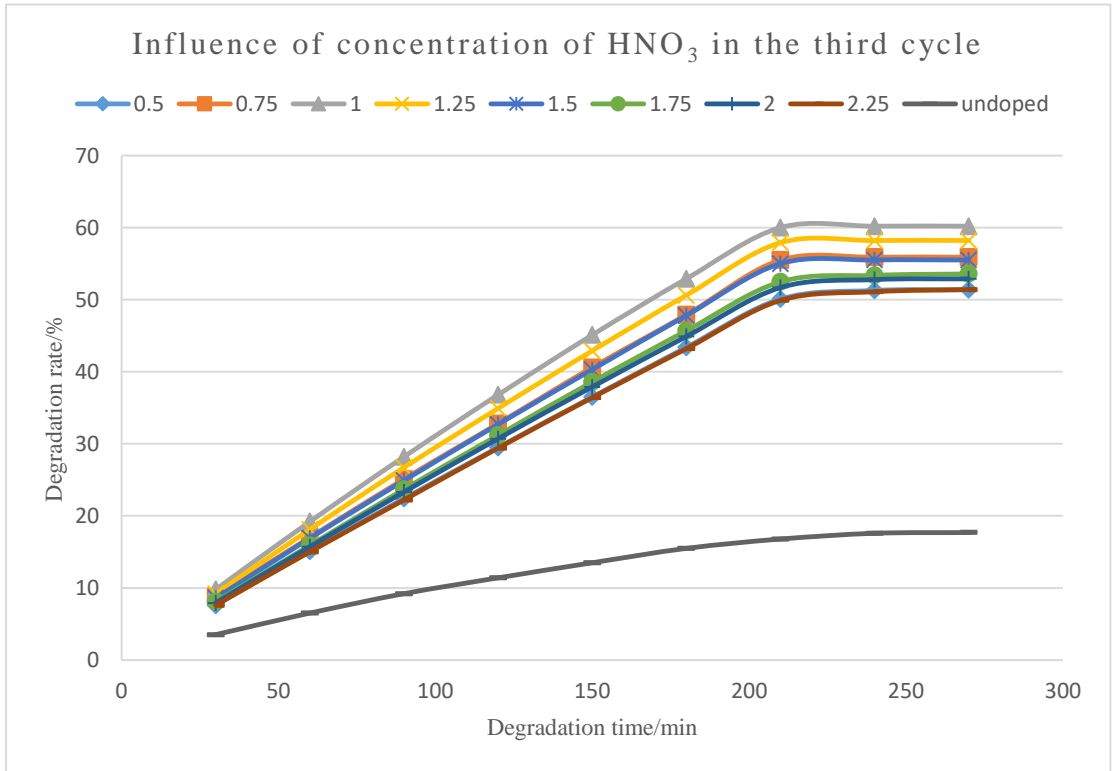
temperature with 400°C. With variation of HNO₃ concentration from 0.5 mol/L, 0.75 mol/L, 1.0 mol/L, 1.25 mol/L, 1.5 mol/L, 1.75 mol/L, 2.0 mol/L to 2.25 mol/L to pretreat. As control group, degradation efficiency of photocatalyst that prepared by undoped TiO₂ loaded on ACF without functionalization was added in the graph and named as undoped. The corresponding degradation efficiency of formaldehyde by the catalyst of mixed materials is presented as follows:



(a)



(b)



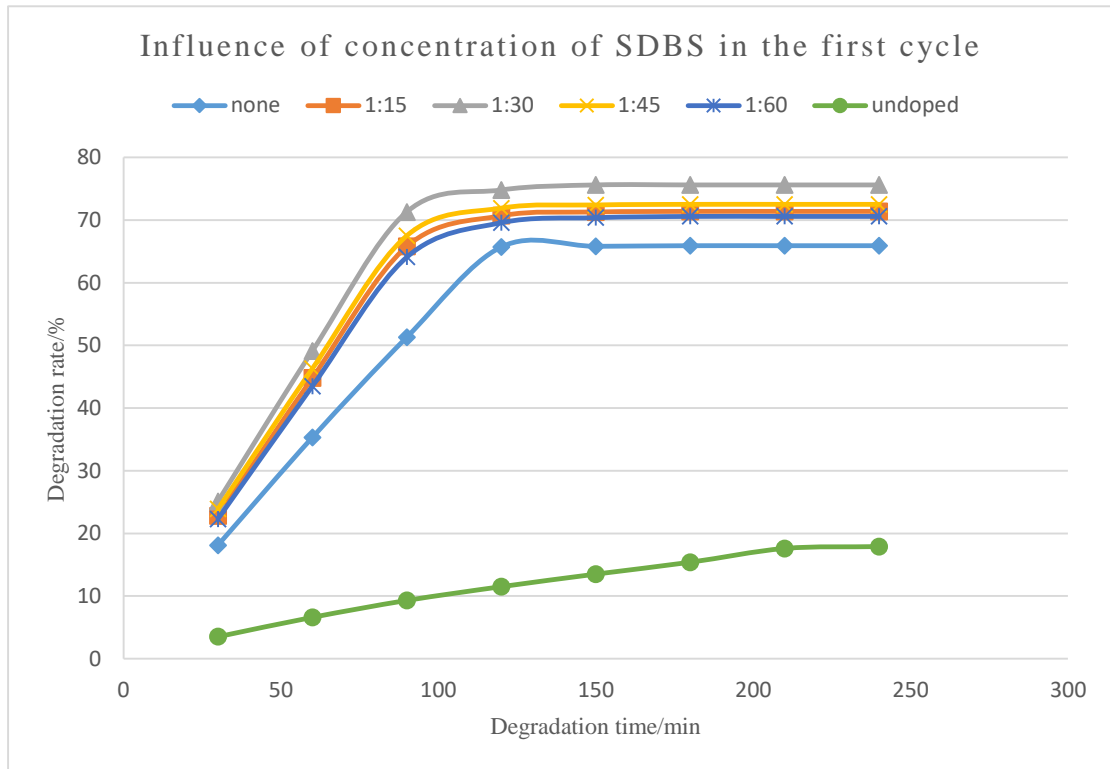
(c)

Fig. 5(a), (b), (c) The influence of the concentration of HNO₃ on the degradation efficiency in three cycles

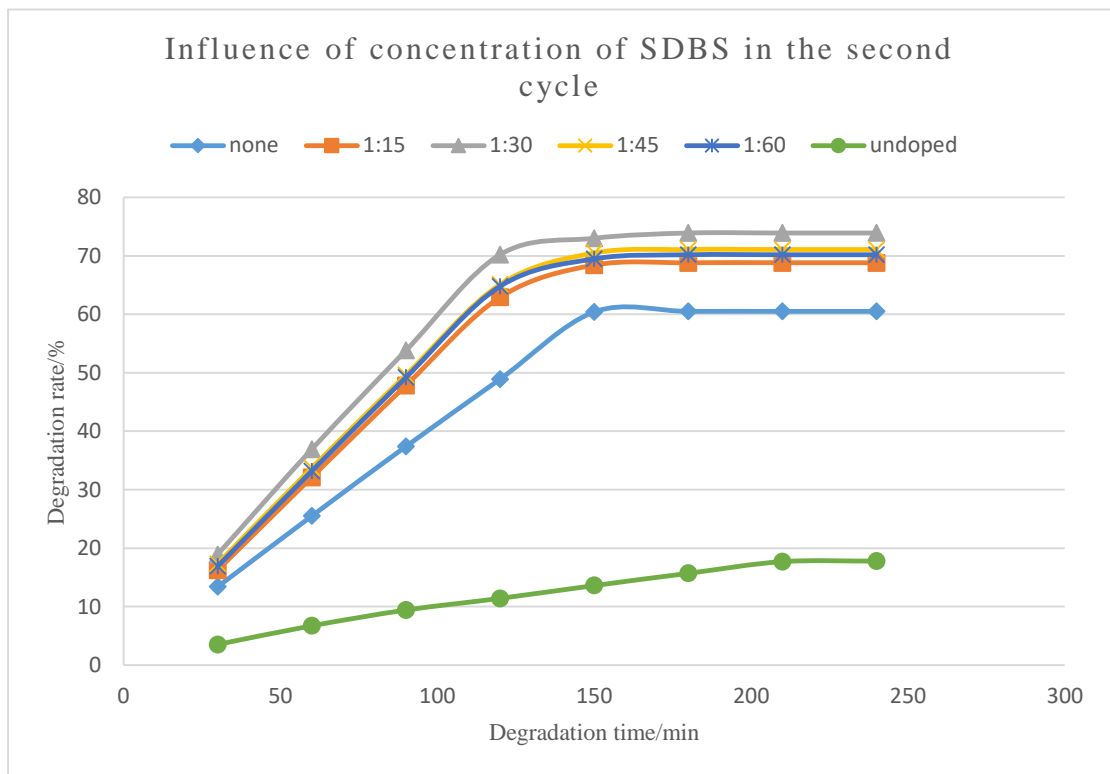
It can be seen from Fig. 5 that the degradation efficiency of formaldehyde increases as an increase of concentration of HNO_3 when the concentration of HNO_3 is below 1.0 mol/L. However, the degradation efficiency of formaldehyde decreases as the concentration of HNO_3 is larger than 1.0 mol/L. The degradation efficiency of formaldehyde is optimal when the concentration of HNO_3 is 1.0 mol/ L. When the concentration of HNO_3 is high, the acid group will clog the pores of AC, which result in the decrease of the specific surface area of AC, and finally affecting the adsorption capacity of the activated carbon fiber.³⁸ However, with too low concentration of HNO_3 , the ACF will not be fully oxidized, results in the formation of insufficient amount of oxygen-containing functional surface groups that are the unfavorable to the adsorption of gaseous formaldehyde. Therefore, HNO_3 at the concentration of 1.0mol/ L HNO_3 is adopted in the pretreatment of ACF in the further experiments.

1.4 Influence of Concentration of Surfactant

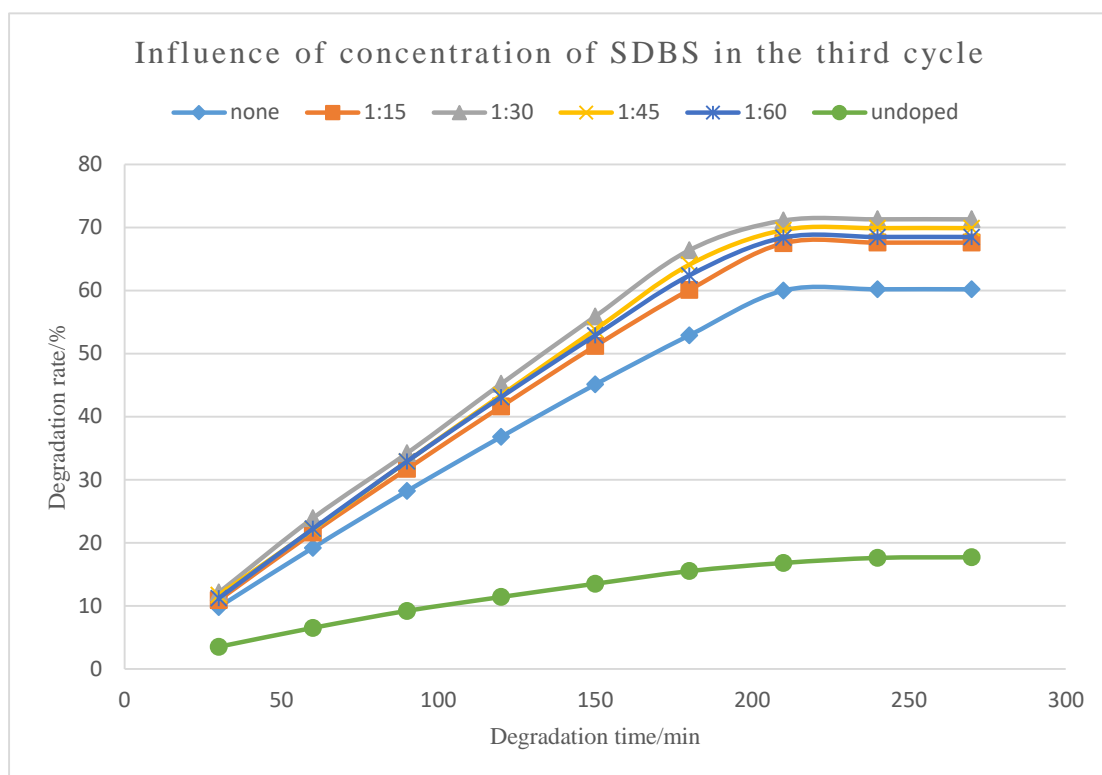
In this section, the effect of concentration of surfactant, sodium dodecyl benzene sulfonate (SDBS), on the degradation efficiency of mixed materials catalysts was investigated. The photocatalyst was prepared from pretreated ACF (1.0 mol/L HNO_3), 12: 7 volume ratio water and TBOT in solution B and calcination temperature with 400°C. The degradation efficiency of formaldehyde when concentrations of no surfactant, mass ratio of SDBS and TBOT are measured to be 1: 15, 1: 30, 1: 45 and 1: 60 after addition of SDBS, the surfactant in solution A with the control of a single variable, as shown in Fig. 6. As control group, degradation efficiency of photocatalyst that prepared by undoped TiO_2 loaded on ACF without functionalization was added in the graph and named as undoped.. The experiment was conducted under the irradiation of fluorescent tube.



(a)



(b)



(c)

Fig. 6 (a), (b), (c) The influence of SDBS concentration on catalytic efficiency in three cycles

It can be seen from Fig. 6 that the degradation efficiency of formaldehyde can be remarkably improved with the addition of surfactant. The degradation rate of formaldehyde will increase with an increase of content of SDBS in a certain range. And the degradation efficiency of formaldehyde is optimal when the concentration ratio of TBOT to SDBS is 1:30. However, if the content of SDBS increased continuously, the degradation efficiency of formaldehyde decreases. This is due to the fact that the anionic surfactant SDBS can acts as a dispersant at a lower content to promote the formation of TiO₂ nanomaterials. Instead, SDBS may act as a surfactant when at a higher content, promoting feature changes in TiO₂ under the environment of high temperature and high pressure⁶⁰. Or the surfactant at a high content may change the hydrolytic condensation environment of the system, thus affecting the catalytic activity of titanium dioxide.

Moreover, based on the experimental results from Fig. 2 to Fig. 6, it can be found that the degradation efficiency of formaldehyde increases with an increase of time, while the catalytic activity of the catalyst of mixed materials reduces with an increase of time.

The reason for that is ACFs have high adsorption rate of formaldehyde with good catalytic effect of the catalyst of mixed materials in a short time and this will help the catalyst to degrade formaldehyde more quickly when the catalyst fails to reach saturation.⁹ However, the catalytic degradation of formaldehyde will be affected when the catalytic degradation time is long enough to facilitate the catalyst to reach saturation.

3.2. Catalyst Characterization

The composition of the crystalline phase and the particle size of the photocatalysts via XRD. It can be seen from Fig.7 that rutile crystal phase that are commonly existed. The peaks observed at 25.42 °, 36.2 °, 48.01 °, 53.1 ° and 55.91 ° represent the anatase crystalline phase.⁴¹ Compared to the undoped one, the diffraction peaks of anatase phase (101) of Fe-N-TiO₂ widened, and their intensity strengthened indicating higher crystallinity. It should be pointed that in codoped TiO₂, Fe³⁺ easily replaces Ti⁴⁺. Also, O²⁻ ions are replaced by N³⁻, thereby oxygen deficiencies are created in the lattice. Moreover, because of the doping of Fe and N atoms, the intensity of TiO₂ strengthened and this leading to higher crystallinity of TiO₂.

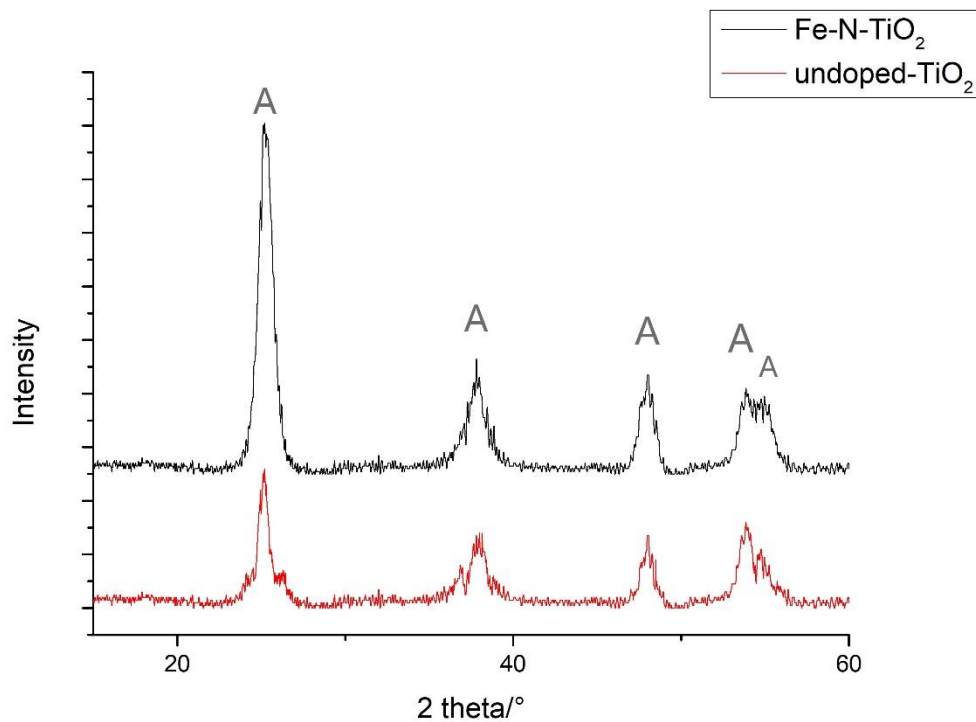


Fig.7 XRD patterns of undoped, co-doped TiO₂

Figure 8 presents SEM micrograph of the undoped TiO₂/ACF and Fe-N-TiO₂/ACF photocatalyst. It can be found that nanoparticles of TiO₂ were obtained effectively via the improved recipe and are equally dispersed on the surface of ACF in the sample. Compared with the undoped one the codoped TiO₂ particles exhibit a more structured shape, this is due to the accession of SDBS which improve the shape of the particles surface and thus help the particles become more globular and disperse uniformly.

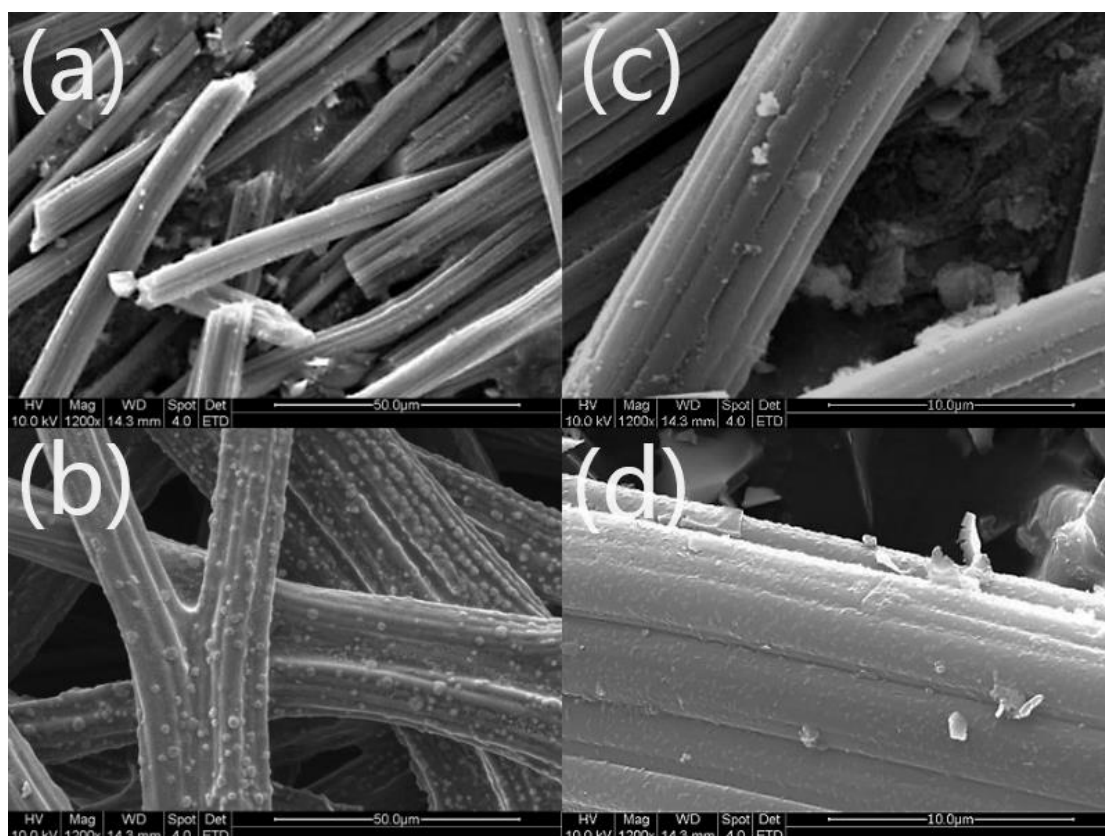


Fig.8 SEM of Fe-N-TiO₂/ACF (a, b) and undoped ACF/TiO₂ (c, d) photocatalyst.

Figure 9 shows the EDS of the Fe-N-codoped TiO₂. It is clear that the peaks represent N, Fe, Ti, respectively, indicating that iron and nitrogen atoms were doped in TiO₂ successfully. The mole ratio of Fe and Ti, N and Ti were nearly 1 % and 25 % respectively.

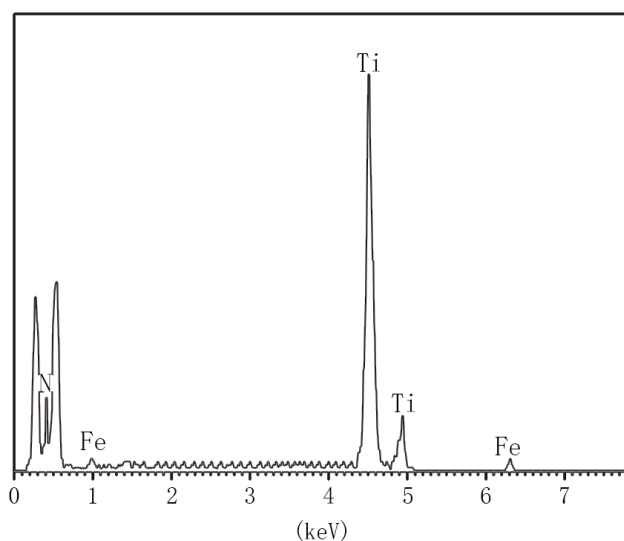


Fig.9 EDS of Fe-N-TiO₂

Table 2 Properties of undoped-TiO₂/ACF, Fe-N-TiO₂/ACF powders

Sample	Anatase size(nm)	Rutile size(nm)	SBET(m ² /g)	Ratio of A and R %
TiO ₂ /ACF	20.4	25.3	1912	90/10
Fe-N-TiO ₂ /ACF	19.5	24.1	1825	78/22

A: anatase crystalline; R: rutile crystalline;

The essence of photocatalytic reaction is the redox reaction of electron and hole which is motivated by light, the surface of catalyst do not have a settled active center . So superficial area of catalyst decide the absorbed dose which means with increase in the superficial area, photocatalytic reaction become more active. Table 1 exhibited that the codoped TiO₂/ACF features a specific surface area of 1825 m²/g compared to undoped one which is 1912 m²/g. The reason that co-doped TiO₂/ACF possess lower specific surface is that pore collapse will happen in ACF when treating with HNO₃.³⁶

Chapter 4. Conclusion

Fe-N-TiO₂/ACF photocatalyst was synthesized via a sol–gel method. And the method was improved by choosing the better volume of hydrolysis water, calcination temperature, concentration of HNO₃ and concentration of SDBS. The photocatalyst was then characterized by XRD, SEM, EDS and BET and evaluated for photocatalytic degradation of formaldehyde. The results showed that:

- (1) The best ratio between hydrolysis water and TBOT is 12:7 and the best calcination temperature is 400 °C;
- (2) Pretreating ACF with HNO₃ can increase number of oxygen-containing functional groups on the surface of ACF and the best concentration of HNO₃ is 1mol/L;
- (3) Adding SDBS as a kind of surfactant in solution A can promote the formation of TiO₂ nanomaterials and the best concentration of SDBS is 1:30 (to TBOT in mass).
- (4) Graph of XRD indicated that compared to the undoped-TiO₂, the diffraction peaks of anatase phase of Fe-N-TiO₂ widened, and their intensity strengthened; Image of SEM showed that the particles of Fe-N-TiO₂ dispersed better on the surface of ACF than that of the undoped one; The graph of EDS showed that Fe and N are doped in TiO₂ successfully; The table of BET exhibited that the Fe-N-TiO₂/ACF features better specific surface area than undoped-TiO₂/ACF.

Compared to previous reported catalysts for degradation of formaldehyde⁴⁻⁷, the product would be easy to recycle and can have greater photocatalytic efficiency for indoor formaldehyde below 20 ppm under visible light irradiation. Subjected to the experiment facility and time, the elements that will influence the photocatalytic activity of Fe-N-TiO₂/ACF are not considered thoroughly. In addition, the photocatalytic efficiency of Fe-N-TiO₂/ACF will decrease distinctly after using three times. We wish to figure it out in the future.

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