

Photodegradation of formaldehyde by activated carbon loading TiO₂ synthesized via microwave irradiation

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Abstract—A microwave-assisted synthetic method to form a series of AC/TiO₂ for application as photocatalytic degradation of formaldehyde (HCHO) is presented. The influence of prepared conditions such as microwave power, microwave time, and the ratio of activated carbon and titanium dioxide sol (AC/TiO₂-sel) on the degradation of HCHO was investigated. HCHO conversion of 58.68% was achieved by AC/TiO₂ at microwave power of 700 W for 15 min with AC/TiO₂-sel ratio of 1 : 2, which maintained multiple properties including high content of anatase and TiO₂ largely distributed on AC without reunion, and possessed abundant functional groups for degradation. The influence of operation parameters on the degradation was also investigated: increasing dosage of catalyst and decreasing the initial concentration of HCHO could increase the conversion of HCHO. Acidic conditions can promote degradation effect. Stronger intensity of UV irradiating could improve efficiency of photocatalytic conversion of HCHO.

Keywords: AC/TiO₂, HCHO, Microwave Irradiation, Photocatalytic Degradation

INTRODUCTION

HCHO is regarded as the major indoor pollutant emitted from the widely used building and decorative materials in airtight buildings, and as a result it is one of the dominating VOCs [1-3]. It can cause adverse impacts on human respiratory system, cardiovascular system and nervous system, and some of them can even cause cancer [4]. Thus, great efforts have been made to reduce the indoor concentrations of HCHO to satisfy the stringent environmental regulations. The physical adsorption of porous materials or combined physical adsorption and chemical reaction by impregnating chemical reagents, such as potassium permanganate and organic amine, was found to be effective for eliminating HCHO emission in a short period [5]. However, the overall efficiency of these adsorbent materials was not so promising due to their limited removal capacities.

Photochemical oxidation is one of the most promising technologies for the abatement of HCHO emission because HCHO can be oxidized into CO₂ over catalysts at much lower temperature than that of thermal oxidation [6-8]. Nanometer TiO₂ is regarded as a most promising photocatalyst. But in the TiO₂ suspension phase system exists the problem of recycling difficulty and easy diffusion of intermediate product of HCHO; and it cannot play a role of degradation when at low concentration of HCHO. So nanoparticles of TiO₂ in aqueous solution can be condensed limiting in application of pollutant treatment. Adding supporter to TiO₂ can possibly increase its photocatalytic efficiency because of the large surface area of the whole composite catalyst. TiO₂ loaded in a carrier has become a current research hot topic [9-11]. Loading materials for

TiO₂ are currently abundant. In the 1980's, Sterte [12] prepared titanium column brace clay porous materials, which have been considered because of some features. Sha et al. [3] reported the HCHO degradation rate of silk mask papers loading nano-TiO₂ was above 60% with reaction time of 180 min. Activated carbon appears to have great advantages over other supports, such as its ability to rapidly adsorb pollutants, as well as its high adsorption capacity due to its high surface area and porosity. Activated carbon can act as an efficient adsorption trap to the organic pollutant, which is then more efficiently transferred to TiO₂ surface, where it is immediately photocatalytically degraded [13,14]. Natalia et al. [15] loaded anatase on activated carbon and studied the photocatalytic effect of phenol. The degradation rate can reach more than 90% while the initial concentration of phenol changes from 35 to 85 mg/L. Huang et al. [13] made an effort to develop photocatalytic TiO₂ crystallite-activated carbon (TiO₂-AC) composites which were evaluated for their adsorption capacity and subsequent photocatalytic activity against HCHO. The result showed the TiO₂-AC composites had much higher formaldehyde-decomposing ability compared to a noncomposite comprising a simple mixture of activated carbon and TiO₂ granules. Lu et al. [16] found that AC/TiO₂ film could increase the photocatalytic reaction rate, as a local high pollutant concentration can be formed on the surface of TiO₂ by the adsorption of AC. Activated carbon chosen as the carrier of TiO₂ has gained more and more attention because of its superior degradation effect.

Traditional method of synthetic loading type of TiO₂ is the heating method. Serpone et al. [17] studied the influence of different conditions of heat treatment on the particle surface features, and showed that with the increasing of calcination temperature, the specific surface area of TiO₂ decreased, and surface adsorption -OH reduced significantly. Reza et al. [18] reported that the Ti/TiO₂ by calcining of 500 °C with 6 h showed an efficient photoelectrocatalytic activity towards HCHO oxidation in a phosphate buffer solu-

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tion. Unfortunately, the process of heating was slow, high energy consuming and non-uniform with the surfaces. And during this conventional process the porous structure of the carrier could be altered, as the microstructure, crystallite size, particle and pore sizes, or electronic structure of the coated TiO₂ photocatalyst [19-22]. Microwave-assisted synthesis loaded TiO₂ materials, in which energy is delivered to the reactants through molecular interactions with the electromagnetic field, have become more attractive in recent years because of high efficiency and stability. He et al. [14] found in the process of microwave-enhanced composite catalyst TiO₂-AC, Rhodamine B (30 mg/L) was almost completely decolorized in 10 min, and the mineralization efficiency was 96.0% in 20 min. Cristina et al. [23] focused on the advantages of microwave-assisted synthesis of TiO₂-coated mesoporous carbon over conventional thermal heating method. Their studies showed that the microwave-assisted synthesis of R/TiO₂ can be completed within a short reaction time, and the nanoparticles' properties were more superior to that prepared by conventional method. However, there are only few recent works applying microwave-assisted synthesis AC/TiO₂ in HCHO photocatalysis.

Our aim was to use microwave-assisted synthesis of AC/TiO₂ to improve the photocatalytic activity of TiO₂ prepared via sol-gel method. XRD, SEM, and FTIR analysis of AC/TiO₂ were conducted, and the effect of preparation conditions and operating parameters on the degradation performance of HCHO was studied. At the same time, the experiments have important scientific significance and theory value on effectively solving the environmental problem.

MATERIALS AND METHODS

1. Microwave-assisted Synthesis AC/TiO₂

The AC powder was added into HNO₃ solution for 24 h, then filtered from the distilled water until it was neutral. It was then dried and stored for use. The TiO₂ were synthesized via sol-gel method. All reagents were of analytical grade and used without further purification. In a typical synthesis process, 30 mL of tetrabutyl orthotitanate (TBOT) was dissolved in anhydrous alcohol (EtOH) in a volume ratio of 1 : 1. This solution was thoroughly stirred for 40 min and named solution A. Solution B was prepared by mixing 14 mL of glacial acetic acid and 7 mL of distilled water in 35 mL of absolute alcohol. Solution B was added to solution A dropwise and continuously stirred for 1 h. Then a pale yellow clear TiO₂ sol was obtained. For the preparation of supported TiO₂ on AC, a specific amount of pretreated AC was added into the titanium sol. After solidification, the mixed powder was calcined at different microwave conditions.

2. Characterization Analysis

The crystal phases of the fabricated samples were analyzed by powder X-ray diffraction (XRD) analysis. XRD was on a Rigaku D/MAX-YA diffractometer with Ni-filtered Cu K α radiation as the X-ray source. Fourier transform infrared spectra (FTIR, Spectrum, AVATAR-360 spectrometer, America Nicolet Company) was used to investigate the transformation of organic group in the sol fabrication process. The surface morphology of the AC/TiO₂ was examined using scanning electron microscopy (SEM) (JSM-6490LV, Japan Electron Optics Laboratory Ltd. Corp., Japan) at accelerated volt-

ages of 15 kV.

3. Photocatalytic Activity

The photocatalytic degradation of HCHO was in a self-restraint container surrounded by several 12 W UV lights. The HCHO solution was dissolved in bi-distilled deionized water to obtain a final concentration of 30 mg/L and which was regulated pH value to 7. AC/TiO₂ (1 g) was added into 30 mL of HCHO solution in 100 mL of conical flask. Prior to the irradiation, the suspension was magnetically stirred at agitation speed 120 rpm in the dark for 30 min to ensure the adsorption equilibrium of HCHO onto the photocatalysts. After equilibrium, the UV light at 256 nm was turned on. The concentration of HCHO was measured after photodegradation.

The conversion (η) of the HCHO is calculated:

$$\eta = \frac{C_0 - C_1}{C_0} \times 100\%$$

where C_0 , C_1 are the initial and degraded concentrations of HCHO, respectively.

RESULTS AND DISCUSSION

1. Catalyst Characterization

1-1. XRD Analysis of AC/TiO₂

X-ray diffraction (XRD) was used to characterize the crystal-

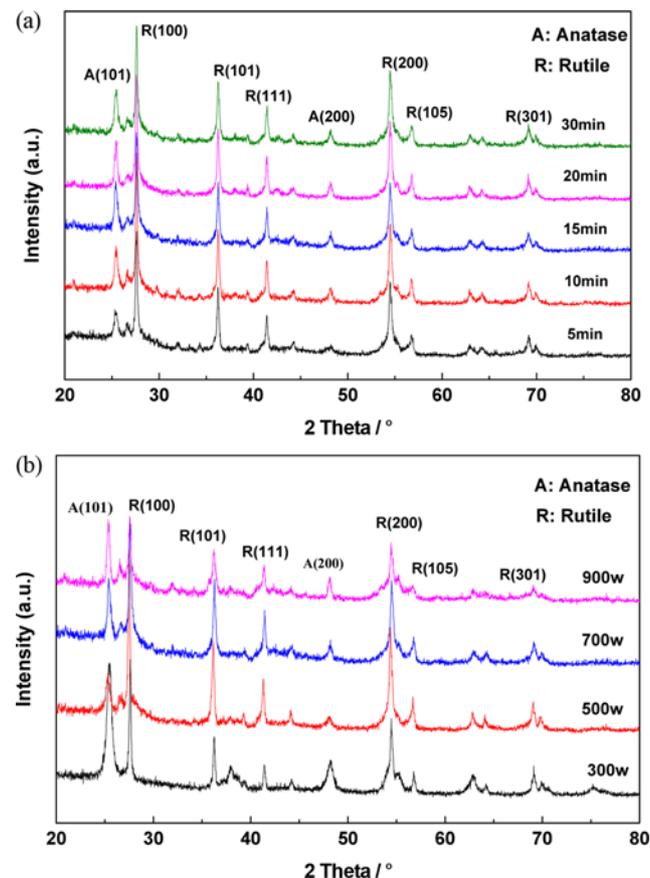


Fig. 1. XRD patterns of AC/TiO₂ prepared at different microwave times at 700 W (a) and prepared at different microwave powers for 15 min (b).

line properties of nano-TiO₂. The XRD patterns of AC/TiO₂ prepared at different microwave times can be seen in Fig. 1(a). The TiO₂-coated AC prepared at different microwave times or powers show the same peaks, with a small difference in peak width. Compared to the database of Joint Committee on Powder Diffraction Standards (JCPDS), the peaks at 27.4°, 36.1°, 41.2°, 54.3°, 56.6° correspond to (100), (101), (111), (200), (105) reflection of rutile, respectively. The TiO₂ anatase phase can be detected in the powder sample after 5 min of microwave (MW) radiation. A strong peak occurs at 25.3° corresponding to the (101) reflection of anatase. From 5 to 15 min, with the increasing MW treated time, the diffraction peaks of anatase (101) became broadened and the intensity markedly increased [23]. The crystallinity of anatase (101) increased and smaller crystallites of TiO₂ on the AC were formed as time progressed. When the microwave time exceeded 15 min, the diffraction peaks of anatase (101) decreased and the crystallite size increased with increasing microwave time because during microwave treatment, the temperature increase over time caused the crystallites to “melt” and agglomerate.

The XRD patterns of AC/TiO₂ prepared at different microwave powers indicate that TiO₂ is a mixture of anatase and rutile structure (Fig. 1(b)). When the power was set at 700 W, the (101) reflection of anatase showed more than the particles prepared at other powers. Even at 300 W, rutile structures were still present. This result is in agreement with the results of other studies: the anatase-type structure easily transforms to rutile phase [24].

1-2. FTIR Analysis of AC/TiO₂

The chemical properties of the synthesized samples investigated via FTIR spectroscopy are presented in Fig. 2. The broad absorption band in the region 3,200 to 3,600 cm⁻¹ demonstrates that the carbon surface is rich in hydroxyl groups; the band was assigned to the stretching vibration of O-H bonds [25]. The 1,610 cm⁻¹ band originates from the stretching vibration of C=C bonds of the AC framework, whereas the 1,456 and 1,392 cm⁻¹ bands are attributed to the O-H bending of carboxyl groups. Once the TiO₂ species were loaded, the intensities of these bands increased. These increased functional groups that are distributed on the AC surface improved the hydrophilicity and wettability, which is advantageous for the adsorption and removal of organics from aqueous solutions. The

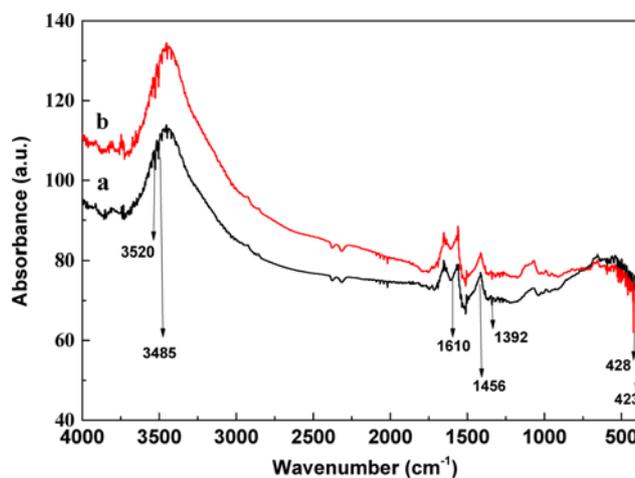


Fig. 2. FTIR transmittance spectrum of AC and AC/TiO₂. (a) is AC, (b) is AC/TiO₂.

broad absorption band in the range of 400 to 800 cm⁻¹ is attributed to the Ti-O and Ti-O-Ti vibration of anatase [26], thereby suggesting that TiO₂ is bonded to the AC surface.

1-3. Surface Morphology Analysis of AC/TiO₂

The morphology of the synthesized samples was studied via SEM, and the SEM images of uncoated and TiO₂-coated AC materials are shown in Fig. 3. The analysis indicated that TiO₂ particles were loaded on AC after the microwave process, thereby causing lightly rough surfaces produced on AC. At the prepared conditions under power of 700 W with 15 min microwave radiation, the photocatalyst seems to completely cover the surface of AC without reunion, even if it is not homogeneous.

2. The Effect of AC/TiO₂ Prepared Conditions on the Degradation of HCHO

2-1. Microwave Power

To investigate the best active catalyst of AC/TiO₂ prepared at different microwave powers (300, 500, 700, and 900 W), catalytic oxidation of 30 mg/L HCHO was performed in 100 mL of conical flask with an AC to TiO₂-sel ratio of 1 : 10. The conversion as a function of reaction time is shown in Fig. 4. The removal rate of HCHO

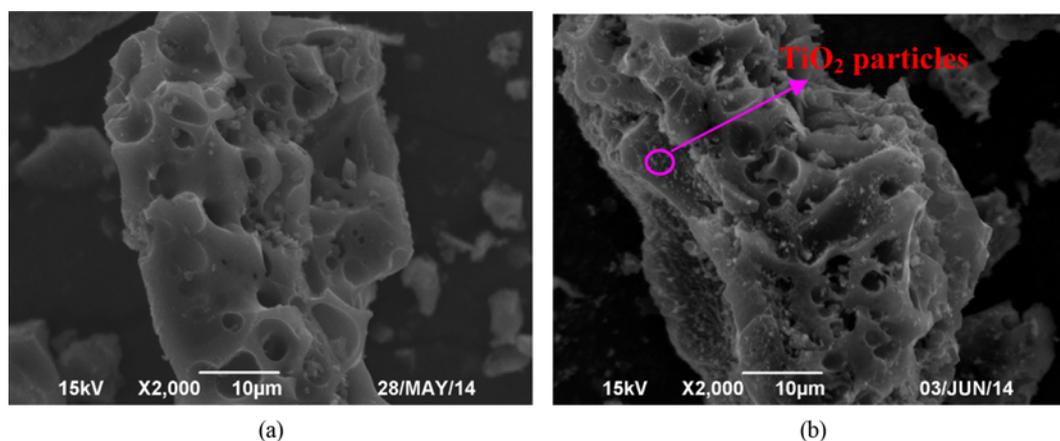


Fig. 3. SEM images of AC and AC/TiO₂. (a) AC, b AC/TiO₂ prepared at 700 W for 15 min.

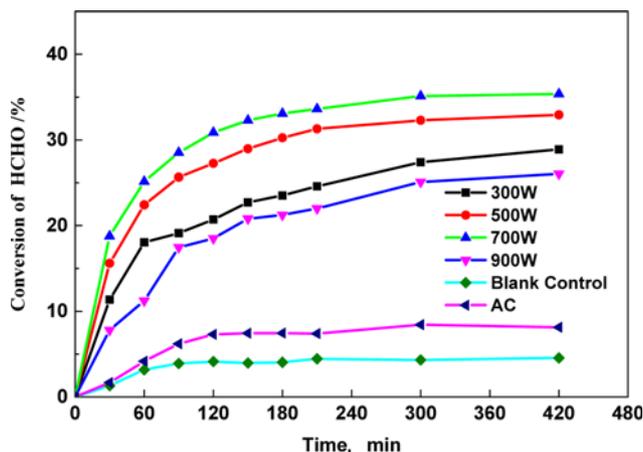


Fig. 4. Effect of microwave power on the properties of AC/TiO₂ prepared with the ratio of AC to TiO₂-sel 1 : 10 and microwave time for 15 min (initial concentration of HCHO solution: 30 mg/L, 1 g AC/TiO₂, pH: 7).

on AC was around 7%, and the self-degradation of HCHO was around 4%. The degradation of HCHO exceeded 20% by AC/TiO₂ prepared for microwave time of 15 min when the reaction reached the balance of 300 min under UV radiation. In conclusion, AC/TiO₂ significantly improved the removal rate of HCHO. This result agrees with the research that the absorption of AC and the catalytic property of TiO₂ have a synergetic effect: AC increases the concentration of HCHO via absorption on its surface, and TiO₂ then regenerates AC by decontaminating HCHO [11]. As listed in Table 1, the microwave heating technique has a better effect in prepared time than the conventional heating method. When the power was set at 700 W, the conversion could be 35.13% in equilibrium, which is better than that at other prepared powers because AC/TiO₂ prepared at 700 W has the most anatase (101) than others, which can be seen from the XRD results. The efficiency of the TiO₂-coated AC samples followed the order: 700 W > 500 W > 300 W > 900 W, while the reaction reached balance.

2-2. Microwave Time

Fig. 5 illustrates the conversion of HCHO as a function of microwave time for AC/TiO₂ prepared at 500 and 700 W. When the AC/TiO₂ spheres were subjected from 5 to 15 min of MW radiation, the conversion of HCHO increased from 13.96 and 17.66 to 25.3 and 27.13%, respectively. When the radiation time was further increased, the conversions decreased. In conclusion, only a few minutes of microwave treatment of AC/TiO₂ powder could improve the crystallinity of the particles and the conversion of HCHO. A

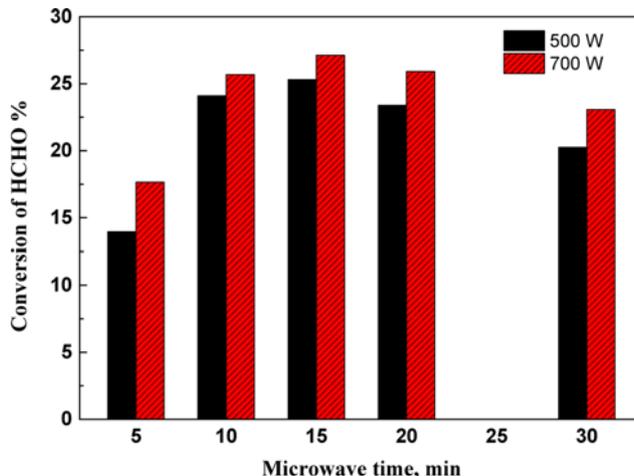


Fig. 5. Effect of microwave time on the properties of AC/TiO₂ prepared with the ratio of AC to TiO₂-sel 1 : 10 (initial concentration of HCHO solution: 30 mg/L, 1 g AC/TiO₂, pH: 7).

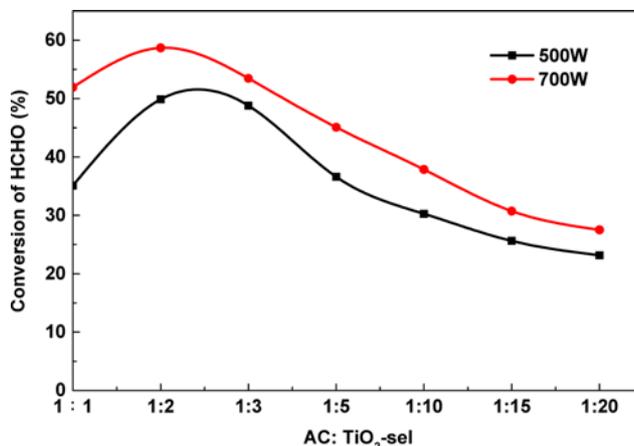


Fig. 6. Effect of AC: TiO₂-sel on the properties of AC/TiO₂ prepared with microwave time for 15 min (initial concentration of HCHO solution: 30 mg/L, 1 g AC/TiO₂, pH: 7).

drastic reduction in the crystallization time allows the specific surface area to retain high values, as seen in the SEM images, and the structural order increased, as seen in the XRD results, which eventually led to a better photocatalytic performance.

2-3. Ratio of AC to TiO₂-sel

AC/TiO₂ was prepared by different ratios of AC and TiO₂-sel and used to study the effect of photocatalytic degradation effect on HCHO. The experimental results are shown in Fig. 6. The results

Table 1. Influence on degradation of HCHO by different kinds of catalyst

| Catalysts | Preparation conditions | Light source | Degradation time (min) | Conversion (%) |
|---|-------------------------------|--------------|------------------------|----------------|
| AC/TiO ₂ This work | Microwave irradiation | UV | 300 | 82.97 |
| TiO ₂ /tourmaline [8] | Conventional heating with 6 h | UV | 360 | 96.32 |
| TiO ₂ /polyester fiber [11] | Conventional heating with 4 h | UV | 120 | Around 30.0 |
| AC/(wood sawdust)/TiO ₂ [13] | Conventional heating with 5 h | UV | 200 | Around 25.0 |
| AC (commercial)/TiO ₂ [27] | Conventional heating with 3 h | UV | 30 | 80.0 |

indicate that the removal rate of HCHO over AC/TiO₂ increased when the ratio of the AC and TiO₂-sel was increased from 1 : 1 to 1 : 2 and then decreased when the ratio was increased from 1 : 2 to 1 : 20, because the adsorption of HCHO mainly occurred on the surface of catalyst and the degradation happened subsequently on TiO₂. Similar results have been found in many studies [8]. The first is activated carbon adsorption HCHO at low concentrations of HCHO. Upon reaching a specific concentration, the TiO₂ began to degrade under UV irradiation. When the ratio of TiO₂ was increased, more TiO₂ particles gathered in the AC channel, thereby promoting the synergy of AC and TiO₂ and accelerating the degradation of HCHO. However, further increasing the content of AC may lead to activated carbon aperture blockage, which results in the decrease in the photocatalytic ability of TiO₂ in the composites.

3. Effect of Operating Conditions on the Photodegradation of HCHO by AC/TiO₂

3-1. Dosage of AC/TiO₂

The influence of dosing quantity of AC/TiO₂ prepared at two different powers on the degradation of HCHO can be seen in Fig. 7. The degradation efficiency of HCHO increased significantly from 30% to 70% when the photocatalyst dosage was increased from 1 to 4 g. It is similar to the report by Qu et al. [7] that the degradation of HCHO increased from 0 to 82.9% when the amounts of N-TiO₂ powder increased from 0 to 5 g, with HCHO initial concentration at 0.98 mg/m³ (about 0.8 ppm at 20 °C), relative humidity at 33%±5%, and illumination intensity at 10,000 lux. When the amount of the AC/TiO₂ powders was increased, the number of electron-hole pairs on the surface also increased. Thus, the photodegradation ratio also increased.

3-2. pH Value of Initial Solution

In Fig. 8, the conversion is higher when the pH of the initial HCHO is acidic, whereas for pH>8, the conversion is very low. As discussed in a previous paper [28], the pH significantly influences the zeta potentials of TiO₂ surface such that when the pH value is low, the zeta level of TiO₂ is low, and TiO₂ particle surface is positively charged because of enhanced protonation. On the one hand,

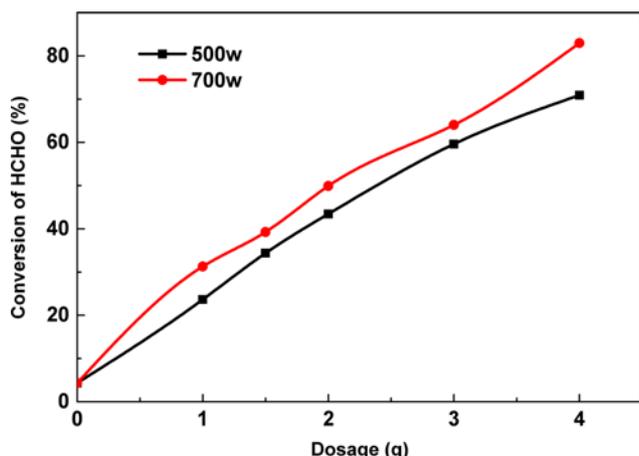


Fig. 7. Effect of dosage on the properties of AC/TiO₂ prepared with the ratio of AC to TiO₂-sel 1 : 10 and microwave time for 15 min (initial concentration of HCHO solution: 30 mg/L, pH: 7).

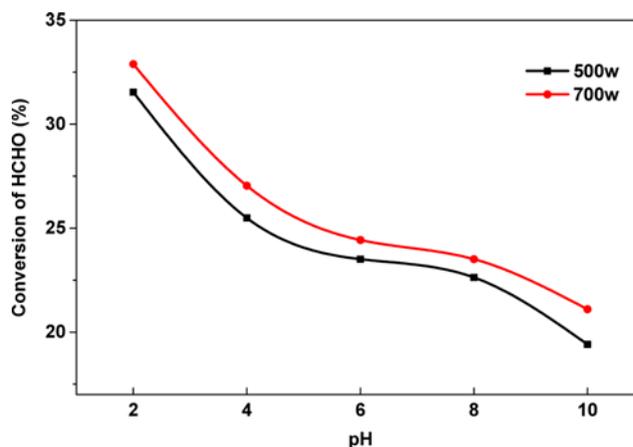


Fig. 8. Effect of pH value of solution on the properties of AC/TiO₂ prepared with the ratio of AC to TiO₂-sel 1 : 10 and microwave time for 15 min (initial concentration of HCHO solution: 30 mg/L, 1 g AC/TiO₂).

the positively charged surface of the catalyst is conducive to electronic transfer to the catalyst surface. On the other hand, HCHO is electronegative after ionization in solution. As such, it can easily migrate to the surface of the positively charged catalyst.

3-3. Initial Concentration of HCHO

The performance of the oxidation catalyst for various HCHO concentrations is worthy of investigation because the HCHO level in the field varies. The catalyst activity at different HCHO concentrations (5 to 50 mg/L) has been examined, and the results are shown in Fig. 9. When the AC/TiO₂ was prepared at 500 W, the conversion of HCHO was 32.49, 30.07, 26.54, 22.15, and 18.48% at 5, 15, 25, 35, and 50 mg/mL, respectively. At 700 W, the HCHO degradation efficiency increased from 19.63 to 36.60% when the HCHO initial concentration was decreased from 50 to 5 mg/L. Therefore, a low initial concentration can improve the degradation efficiency of HCHO. This is parallel to the result in Qi et al's study [29], where the HCHO initial concentration increased from 1.84 to 24 mg/m³

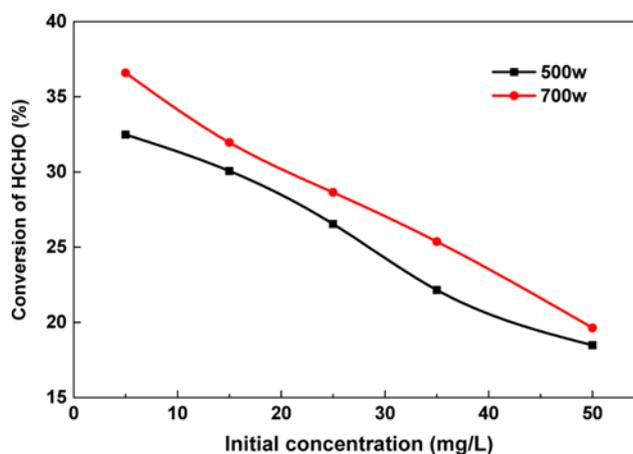


Fig. 9. Effect of initial concentration on the properties of AC/TiO₂ prepared with the ratio of AC to TiO₂-sel 1 : 10 and microwave time for 15 min (1 g AC/TiO₂, pH: 7).

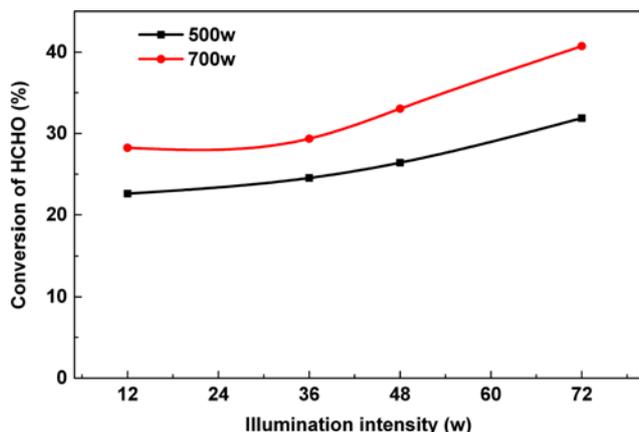


Fig. 10. Effect of light intensity on the properties of AC/TiO₂ prepared with the ratio of AC to TiO₂-sel 1 : 10 and microwave time for 15 min (initial concentration of HCHO solution: 30 mg/L, 1 g AC/TiO₂, pH: 7.0).

(about 1.50–19.52 ppm at 20 °C) and the HCHO degradation efficiency decreased from 72 to 43.4% with a flow rate of 5 L/min. In a liquid-phase photocatalyst, the collision frequency between radicals and HCHO affected the removal efficiency. When formaldehyde molecule reaches the catalyst surface, photo-oxidation occurs. The number and energy of liquid-phase reactive radicals in the reaction area did not change at a fixed UV irradiation. Therefore, when the initial HCHO concentration was increased, HCHO obtained less energy, thereby resulting in low HCHO removal.

3-4. Light Intensity

To investigate the influence of the UV intensity on the photocatalytic efficiency, the experiments were performed using a 12 to 72 W ultraviolet tube. The experimental results are shown in Fig. 10. Increasing the power of the light could increase the degradation of HCHO by AC/TiO₂ at a given wavelength light source. For the illuminated photodegradation reaction, the influence of light intensity is seldom discussed. Qu et al. [7] studied the effect of light illumination on the photodegradation of HCHO by a nitrogen-doped TiO₂ photocatalyst. With HCHO initial concentration at 0.98 mg/m³ (about 0.8 ppm at 20 °C), the degradation increased linearly from 25.5% to 59.6% alongside an incrementing illumination intensity of 0 to 30,000 lux and stabilized thereafter. Yu et al. [30] found an increasing NO_x conversion rate when the light intensity was increased from 1.0 to 13.0 W/m² according to a logarithmic relation. This result is determined by the photocatalytic mechanism: increasing the light intensity can increase the number of effective photons. As such, HCHO molecules can easily absorb light quanta. On the other hand, when the light intensity is increased, more electron hole pairs are produced, and the probability of electron transition also increases, which accelerates the reaction on the surface of the catalyst.

CONCLUSIONS

Microwave-assisted synthesis of AC/TiO₂ prepared at 700 W for 15 min presents good conversion of HCHO under UV irradiation. Based on XRD and SEM results, the AC/TiO₂ contains anatase

(101) crystal, and TiO₂ was dispersed abundantly in the AC. FTIR analysis shows that the content of O-H is greater on the AC/TiO₂ surface than AC. These results explain that AC/TiO₂ has good photocatalytic performance. When the ratio of AC: TiO₂-sel was 1 : 2, the effect of AC/TiO₂ on the degradation of HCHO was at its best. At the same time, the experiments showed that increasing the dosage of the catalyst and decreasing the initial concentration of HCHO could increase the conversion of HCHO. AC/TiO₂ has a better adsorption degradation effect at acidic conditions. Within a specific range of UV radiation, a strong intensity of UV indicates a good effect of photocatalytic conversion of HCHO.

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