

Developing Cu-Mesoporous TiO₂ Cooperated with Ozone Assistance and Online-Regeneration System for Acid Odor Removal in All Weather

Yuchih Lin, Chung-Liang Chang, Hong-Yi Cao, and Sheng-Hsuan Hsiao

Abstract—Cu-mesoporous TiO₂ is developed for removal acid odor cooperated with ozone assistance and online-regeneration system with/without UV irradiation (all weather) in study. The results showed that Cu-mesoporous TiO₂ present the desirable adsorption efficiency of acid odor without UV irradiation, due to the larger surface area, pore size and the additional adsorption ability provided by Cu. In the photocatalysis process, the material structure also benefits Cu-mesoporous TiO₂ to perform the more outstanding efficiency on degrading acid odor. Cu also postponed the recombination of electron-hole pairs excited from TiO₂ to enhance photodegradation ability. Cu-mesoporous TiO₂ could gain the conspicuous increase on photocatalysis ability from ozone assistance, but without any benefit on adsorption. In addition, the online regeneration procedure could process the used Cu-mesoporous TiO₂ to reinstate the adsorption ability and maintain the photodegradation performance, depended on scrubbing, desorbing acid odor and reducing Cu to metal state.

Keywords—mesoporous material, photocatalyst, adsorption, regeneration usage, photocatalytic ozonation

I. INTRODUCTION

TAIWAN is famous in its semiconductor and opti-electronic industries of high export/import trade markets. A greater part of semiconductor and opti-electronic industry in Taiwan are located at Hsinchu Science-Based Industrial Park (SBIP), which is the so called “Taiwan Silicon Valley”. However, some of odorous problems from the above industries are caused by the volatile organic compounds (VOCs), and acid material. These odorous exhausts would persecute residents’ health and lower the environmental quality. For abating the air pollution from these manufactures, the regulations—“Air Pollution Control and Emission Standards for Semiconductor Industries”, and “Air Pollution Control and Emission Standards for Opti-electronic Industries” have been promulgated in 1999 and 2006, respectively. In addition, Taiwan EPA revised the “The Standard of Air Pollutant Emission from the Stationary Source”, and promoted “The Standard of Odorous Emission” stricter in September, 2007 [1].

Yuchih Lin, the corresponding author, is an Associate Professor at Department of Environmental Engineering and Health, Yuanpei University, Hsin-Chu City 300 Taiwan (phone:+886-5381183 ext.8479; fax:+886-6102337; email:yuchihlin@mail.ypu.edu.tw)

Chung-Liang Chang is an Associate Professor at Department of Environmental Engineering and Health, Yuanpei University, Hsin-Chu City 300 Taiwan (email: clchang@mail.ypu.edu.tw)

Hong-Yi Cao is an undergraduate student at Department of Environmental Engineering and Health, Yuanpei University, Hsin-Chu City 300 Taiwan (email: erebus920047@hotmail.com)

Sheng-Hsuan Hsiao is an undergraduate student at Department of Environmental Engineering and Health, Yuanpei University, Hsin-Chu City 300 Taiwan (email: zero200293@hotmail.com)

Due to stringent environmental regulations in Taiwan as well as increasing concerns from neighboring residents, the request of air quality becomes more and more, especially the deodorization in the atmosphere. The deodorization methods include adsorption [2,3], absorption [4], catalytic oxidation [5-7], plasma destruction [8], and advanced oxidation [9] etc.. These processes will be operated on the high efficiency. But the traditional adsorbent will be replaced frequently on the operation; the high voltage in plasmas destruction and high temperature in catalytic oxidation will cause the potential risk for the staffs. In addition, the large oxidant tank is necessary in advanced oxidation, but the tank occupied the factory space and the oxidant leak will be taken precautions. Titanium dioxide (TiO₂) has been widely applied and proven efficiently on decontamination, sterilization and deodorization, as well as removing NO_x and volatile organic compound (VOCs) [10-12]. In presence of ultra violet (UV) irradiation, TiO₂ excites electron-hole pairs that can disrupt molecular structure of target pollutant, breaking its bonds into inorganic material. Recently, the photodecomposition efficiency of pollutant on TiO₂ can be enhanced by the addition of porous characteristic. Pollutant would not only be removed by adsorption, but the illuminated area and photocatalysis performance also could be enhanced due to the increasing surface area of TiO₂[13-15]. In addition, the better porous structure and larger surface area contribute mesoporous TiO₂ to have the great potential for photocatalysis improvement[16]. Shamaila et al.[17] had used P123 and PEG600 to synthesize mesoporous TiO₂ of single and dual templates, respectively. Parts of their results showed the photocatalysis performance of mesoporous TiO₂/P123 is better than that of mesoporous TiO₂/PEG600 and Degussa P25, and proved the template was the effect factor on mesoporous TiO₂ for photodegrading pollutant.

Recently, the copper has been modified on the surface area of TiO₂ instead of noble metal, due to it being more economical. Tseng et al. [18] indicated Cu/TiO₂ could produce more methanol yield than P25 in an aqueous solution of CO₂ under UV illumination. Cu-mesoporous TiO₂ was also synthesized and showed the conspicuous ability for photodegrading dye under visible light irradiation[19]. In photocatalysis process, Copper could also postpone the recombination between electrons and holes excited from TiO₂ under UV illumination, and then increase the photocatalytic property[20]. Furthermore, Cu²⁺ ion acted on the competent catalyst to enhance photocatalysis performance, no matter in oxidation and reduction reactions [21-23].

In study, Cu-mesoporous TiO₂ is developed for removal acid odor cooperated with ozone assistance and online-regeneration system with/without UV irradiation (all weather). The compound was targeted as acetic acid, a low odor-threshold compound, which is the essential in the etching process of semiconductor and opti-electronic industries and usually

detected in atmosphere of the science industries park. It is expected that the porous characteristic of mesoporous TiO₂ deals acid odor with the adsorption, and the copper treats acid odor with a chemical absorption without UV irradiation; Cu-mesoporous TiO₂ also exert the photocatalytic decontamination with UV irradiation. This method would improve the service life of the adsorption medium, and enhance the photocatalysis performance. The effects of ozone assistance and online- regeneration procedure on the photodegradation efficiency are also discussed in this study.

II. EXPERIMENTAL METHOD

A. Preparation of Cu-mesoporous TiO₂

The synthesis process of mesoporous TiO₂ was referred to the Yu et al.'s method. In briefly, 0.97g F127 was dissolved in 20ml N-Butyl Alcohol under vigorous stirring until solution as clear. Titanium tetraisopropoxide(TTIP) were dropped into the F127 solution, continued to stir for the other one hour. Next, the hydrochloric acid solution, consisting of 2.9ml 35% HCl and 3.9ml di-water, was added to the above solution under stirring for an additional 30min. Then, the solution was extended sufficiently as a uniform thin layer in petri dish, treated on the 75% of environmental humidity for one day and 25°C for four days in order to aging. After dried at 140°C for two hours, 200°C for two hours, calcined at 400°C for four hours, and cooled to room temperature, the mesoporous TiO₂ could be obtained. Cu-mesoporous TiO₂ was synthesized via the photoreduction method. Mesoporous TiO₂ was added in the cupric nitrate solution, stirred with a lamp of 10W-UVA irradiation for 30min. After washing out the acidity, filtering and drying, the Cu-mesoporous TiO₂ could be obtained. The stoichiometric weight ratio of Cu and TiO₂ was 0.02: 1.

B. Characterization

The specific surface area of the photocatalyst was determined by the BET method using nitrogen adsorption-desorption isotherms (Micromeritics ASAP 2020, USA). The crystalline structure of the photocatalyst was observed by powder x-ray diffraction (XRD, Bruker, D8 Discover, Germany), and surface observations were obtained by transmission electron microscope (TEM, JEOL JEM-2000EX, Japan).

C. Photodegradation efficiency of acid odor via Cu-mesoporous TiO₂ testing system

The removal efficiency of acid odor was investigated in the presence (light condition) and absence (dark condition) of UVA irradiation. An 8W UVA light (Philips, Netherlands), with an outer diameter of 1.6 cm and length of 14.6 cm, was placed in the central part of the reactor.

The reactor was made of Pyrex glass with an inner diameter of 2 cm and a length of 15 cm. The catalyst (0.1 ± 0.005 g) was coated onto the inner wall of the reactor. The reactor was then ready for the subsequent catalysis test after being dried at 110 °C for 8 h and cooled to ambient temperature.

The acetic acid and relative humidity in the flow was obtained by passing the air through a midjet impinger. The ozone generator (TR300, Tairex) was used to produce ozone.

The acetic acid, moisture, ozone and the dilution flow were controlled by mass flow controllers (5850E, BROOK U.S.A), respectively. The total flow rate and acetic acid concentration, flowing into the reactor were 2lpm(0.11m/s of linear velocity), and 50ppmv, respectively. All experiments were performed with a photocatalysis reactor, which was placed in the thermostat. The acetic acid concentrations at the inlet and the outlet of the reactors were analyzed by acid-gas analyzer (B12 2-wire gas transmitter, ATI, USA), relative humidity of the inlet flow was measured using humidity meter (TES-1361C, TES electrical electronic Corp., Taiwan), and the ozone concentration was analyzed by ozone analyzer (Model 49i, Thermo Scientific, USA). The photodegradation efficiency of acetic acid was determined from a percentage, which was the difference between inlet and outlet concentration divided by the inlet concentration.

III. RESULTS AND DISCUSSIONS

A. Material analysis

TABLE I
 MATERIAL CHARACTERISTICS OF PHOTOCATALYST OBTAINED FROM N₂
 ADSORPTION/DESORPTION AND XRD

Photocatalyst	BET Surface area (m ² /g)	Average Pore Size (nm)	Fraction of Rutile Phase (%)	d (nm)
TiO ₂	33.24	2.5	0	33.9
Mesoporous TiO ₂	101.75	4.9	27.6	18.6
Cu-Mesoporous TiO ₂	99.86	5.1	27.8	18.8

The surface area of TiO₂, mesoporous TiO₂ and Cu-mesoporous TiO₂ were 33.24, 101.75 and 99.86 m²/g, listed in Table I; The surface area of mesoporous TiO₂ was enhanced by added F127 template in the synthesis procedure, and the three times the value of TiO₂. Cu modification on mesoporous TiO₂ didn't decrease the surface area sufficiently due to the low dosage of 2wt% Cu for TiO₂. Each average pore size of photocatalyst was calculated from the Equation (1)

$$\text{Average pore size} = \frac{4 \times \text{pore volume}}{\text{surface area}} \quad (1)$$

the pore volume of Cu-mesoporous TiO₂ didn't decrease with lowering surface area, thus the its average pore size is little larger than that of mesoporous TiO₂.

The crystalline structure of TiO₂, mesoporous TiO₂ and Cu-mesoporous TiO₂ measured by XRD, illustrated on Fig. 1.

The TiO₂ was characterized as the pure anatase phase, both mesoporous TiO₂ and Cu-mesoporous TiO₂ are characterized as the anatase and rutile phase, decided according JCPDS 84-1285 and 82-0514. The intensity percentage of rutile divided by anatase was calculated Equation (2) according [24]

$$X = \frac{1}{1 + 0.8 \left(\frac{I_A}{I_B} \right)} \quad (2)$$

Where IA is the integrated (101) intensity of anatase and IR is the integrated (110) intensity of rutile; the crystal size (d) of the

photocatalysis was determined by Debye Scherrer equation. Fraction of rutile phase in mesoporous TiO₂ and Cu-mesoporous TiO₂ were 27.6 and 27.8 %, respectively.

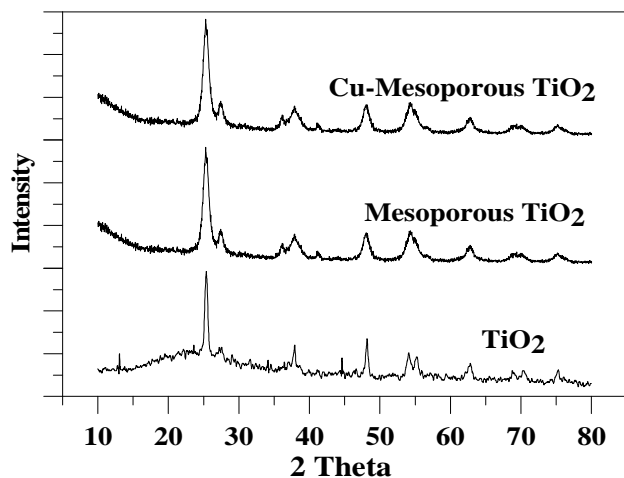


Fig. 1 XRD spectra of TiO₂, mesoporous TiO₂ and Cu-mesoporous TiO₂

This result indicated Cu modified on mesoporous TiO₂ via photoreduction process didn't alter the matrix structure. There is no obvious peak of Cu in the XRD spectra because of the low Cu dosage. The crystallite size of TiO₂, mesoporous TiO₂ and Cu-mesoporous TiO₂ were 33.9, 18.6, and 18.8 nm. Cu modified on mesoporous TiO₂ via photoreduction process didn't also influence the crystallite size. The crystallite size of mesoporous TiO₂ was smaller than that TiO₂ might be contributed to the longer ageing period and self-assembly procedure between surfactant and Ti source.

In Figure 2, the TEM image indicated that Cu-mesoporous TiO₂ still sustained the straight-row ordered structure after photoreduction modifying process. The actual crystal size illustrated in the TEM was less than crystal size (d) calculated from the Debye Scherrer equation according XRD data. This situation was tallied with the result of Yu et al., they describe that the crystal size (d), calculated from the Debye Scherrer equation, represented the theoretical crystal dimension along (101) plane of anatase phase.

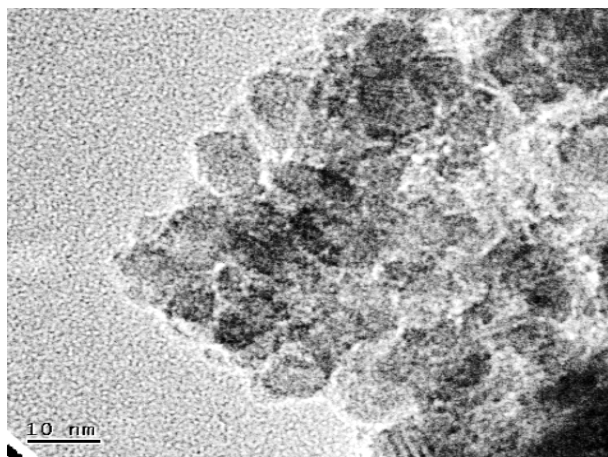


Fig. 2 TEM image of Cu-mesoporous TiO₂

B. Acid odor removal via the adsorption mechanism on photocatalyst

The adsorption breakthrough curves of acid odor among the each photocatalyst were listed on Fig. 3.

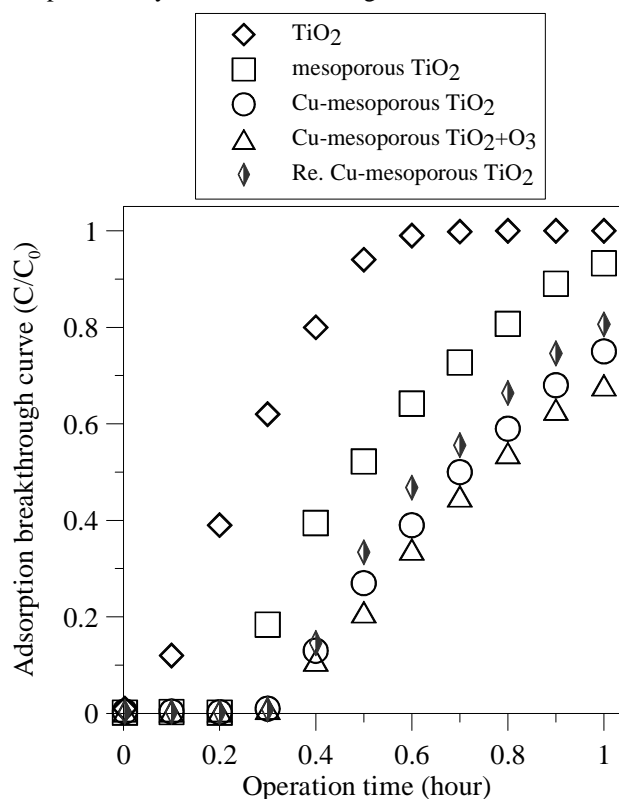


Fig. 3 Comparison the adsorption performance among each photocatalyst for acid odor

Operated on the 0.11m/s of linear velocity and 50ppm of acetic acid, the 0.1g TiO₂ coated on the inner wall of reactor reached on the adsorption breakthrough point within 5min and saturated adsorption within 40min.

As referred to in Table I, the BET surface area of mesoporous TiO₂ was 3 times value of TiO₂, and then mesoporous TiO₂ showed the better adsorption ability. The adsorption efficiency of acid odor on mesoporous TiO₂ could maintain above 90% until 15min, the mesoporous TiO₂ presented the saturated adsorption after operated at 1 hour. Thus, the adsorption efficiency of the porous materials was influenced by an increase in the surface area and pore size.

Modifying Cu on the surface supported mesoporous TiO₂ as functional filter, and further enhanced the original removal efficiency of acetic acid due to Cu reacting with acetic acid. The adsorption breakthrough point of acid odor on Cu-mesoporous TiO₂ was prolonged, and happened on 25min of operating time. Adsorbing after 1hour, Cu-mesoporous TiO₂ still had the 30% removal efficiency for acid odor. The very little difference of material characteristics, listed in Table I, between mesoporous TiO₂ and Cu-mesoporous TiO₂ was deserves to be mentioned, the pore and crystal structure of mesoporous TiO₂ modified via photoreduction method weren't destruct due to the operating at normal temperature and pressure, and modified metal anchored only on the surface.

In addition, the appropriate Cu modification dosage on the mesoporous TiO₂ didn't block the surface area. Ozone assisting Cu-mesoporous TiO₂ for acid odor removal was also discussed in this study; however the adsorption efficiency of acid odor on Cu-mesoporous TiO₂ could not be profited by adding 10ppm ozone obviously. After processing adsorption of several times, the adsorption and absorption efficiency of acid odor on Cu-mesoporous TiO₂ would be saturated and decayed, respectively. The regeneration procedure of used photocatalyst processed online had been developed by our previous study [25]. Briefly describe the procedure and mechanism: Infusing the moisture flow into the reactor, the absorbed acid odor would be scrubbed and taken off from the surface of Cu-mesoporous TiO₂; then infusing the other dry flow, lighting on the UV lamp and increasing temperature at 70°C, the adsorbed acid odor would be desorped due to the heat. The reacted Cu in the oxidized state would be reduced to original metal state, because obtaining the electron excited from the mesoporous TiO₂ under UV irradiating. Thus the removal ability of regenerated Cu-mesoporous TiO₂ for acid odor could be reinstated, illustrated in Fig.4.

C. Acid odor removal via the degradation mechanism on photocatalyst

After adsorping for 1hour, the UV lamp was lighted up in order to photodegrading acid odor. The photodegradation efficiencies of acid odor on each photocatalyst, which were gotten on the 1 hour after lighting UV lamp up, were illustrated on Fig. 4. Photodegradation efficiency of acid odor on TiO₂ was only 7%, operated on the set flowrate and concentration. However, the larger surface area and more porous characteristic could promote between the target pollutant and photocatalyst, the more pollutant would be adsorped and photodegraded on the surface of mesoporous TiO₂. Thus the photocatalysis ability of mesoporous TiO₂ could be improved and showed 5 times the degradation efficiency of TiO₂.

In addition, the better performance of mesoporous TiO₂ was also contributed to the 27.6% fraction of rutile phase, the appropriate ratio of rutile and anatase phase in TiO₂ was verified to profit the VOCs photodegradation [26].

The photodecomposition efficiency of pollutant on Cu-mesoporous TiO₂ was better than that of the other materials. Postponing the recombination between electrons and holes is the role that Cu enhances the photocatalysis. 10ppm Ozone assisting in the photocatalysis process via Cu-mesoporous TiO₂ enhanced degradation efficiency to 60% distinctly, better than the single photocatalysis process. Under UV irradiation and photocatalysis via Cu-mesoporous TiO₂, free oxygen radical decomposed from ozone was accelerative and assisted the acid odor destroyed. The regeneration Cu-mesoporous TiO₂ maintained the fine performance for degrading acid odor, but the lowering efficiency compared to the fresh one was the origin of some incomplete regenerated Cu.

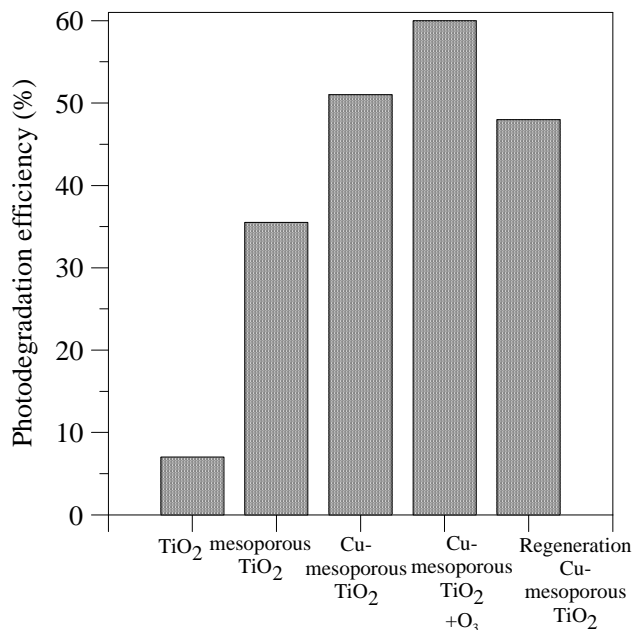


Fig. 4 Comparison the degradation performance among each photocatalyst for acid odor

IV. CONCLUSION

This study synthesized Cu-mesoporous TiO₂ to remove and degrade acid odor, acetic acid, which is usually detected in atmosphere of the science industries park. Without UV irradiation, TiO₂, mesoporous TiO₂ and Cu-mesoporous TiO₂ were compared for the odor removal via adsorption. Owing to dual mechanisms of adsorption and absorption, Cu-mesoporous TiO₂ showed the best adsorption efficiency of acid odor among the tested photocatalyst. The excellent adsorption performance was contributed to the larger surface area and pore size, and the additional absorption ability was provided by the reaction between Cu and acid odor. In the adsorption process, infusing ozone wasn't effective in assisting the increase of acid odor removal.

In the following photocatalysis process, Cu-mesoporous TiO₂ still presented the more outstanding performance on degrading acid odor. The larger surface area and more porous characteristic of Cu-mesoporous TiO₂ not only promote the interaction between target pollutant and active cite, but Cu also postponed the recombination of electron-hole pairs, and improved photodegradation efficiency of acid odor. In addition, 27.6% fraction of rutile phase in Cu-mesoporous TiO₂ also enhanced the performance more than TiO₂ in pure anatase phase. Ozone assistance could help Cu-mesoporous TiO₂ to gain the conspicuous increase on photocatalysis ability. The photodegradation efficiency of acid odor could be upto 60%. This was because that the free oxygen radical, decomposed from ozone under UV irradiation and photocatalysis via Cu-mesoporous TiO₂, assisted the acid odor destroyed. By means of scrubbing, desorping acid odor and reducing Cu to metal state, the online regeneration procedure could reinstate the adsorption capacity of used Cu-mesoporous TiO₂, and furthermore help used Cu-mesoporous TiO₂ to maintain the fine photodegradation efficiency of acid odor.

The removal performance of Cu-mesoporous TiO₂ for acid odor was present, no matter illuminate with or without the UV lamp; and the regeneration procedure of used photocatalyst could be processed online for reinstating the fine ability. Thus, the novel photocatalysis technology, developed in this study, can act as a foundation for developing effective device of indoor air clean in the all-weather.

ACKNOWLEDGMENT

We deeply appreciated the National Science Council, Taiwan for the financial support (NSC 99- 2221- E- 264- 004- MY3) in this study.

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