Developing Cu-Mesoporous TiO$_2$ Cooperated with Ozone Assistance and Online- Regeneration System for Acid Odor Removal in All Weather

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Abstract—Cu-mesoporous TiO$_2$ 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 TiO$_2$ present the desirable adsorption efficiency of acid odor without UV irradiation, due to the larger surface area, pore sizeand the additional absorption ability provided by Cu. In the photocatalysis process, the material structure also benefits Cu-mesoporous TiO$_2$ to perform the more outstanding efficiency on degrading acid odor. Cu also postponed the recombination of electron-hole pairs excited from TiO$_2$ to enhance photodegradation ability. Cu-mesoporous TiO$_2$ 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 TiO$_2$ to reinstate the adsorption ability and maintain the photodegradtion performance, depended on scrubbing, desorping 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].

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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], absoption [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 (TiO$_2$) has been widely applied and proven efficiently on decontamination, sterilization and deodorization, as well as removing NOx and volatile organic compound (VOCs) [10-12]. In presence of ultra violet (UV) irradiation, TiO$_2$ 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 TiO$_2$ 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 TiO$_2$[13-15]. In addition, the better porous structure and larger surface area contribute mesoporous TiO$_2$ to have the great potential for photocatalysis improvement[16] . Shamaila et al.[17] had used P123 and PEG600 to synthesize mesoporous TiO$_2$ of single and dual templates, respectively. Parts of their results showed the photocatalysis performance of mesoporous TiO$_2$/P123 is better than that of mesoporous TiO$_2$/PEG600 and Degussa P25, and proved the template was the effect factor on mesoporous TiO$_2$ for photodegrading pollutant.

Recently, the copper has been modified on the surface area of TiO$_2$ instead of noble metal, due to it being more economical. Tseng et al. [18] indicated Cu/TiO$_2$ could produce more methanol yield than P25 in an aqueous solution of CO$_2$ under UV illumination. Cu-mesoporous TiO$_2$ was also synthesized and showed the conspicuous ability for photodegradating dye under visible light irradiation[19]. In photocatalysis process, Copper could also postpone the recombination between electrons and holes excited from TiO$_2$ under UV illumination, and then increase the photocatalytic property[20]. Furthermore, Cu^{2+} ion acted on the competent catalyst to enhance photocatalysis performance, no matter in oxidation and reduction reactions [21-23].

In study, Cu-mesoporous TiO$_2$ 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 TiO_2 deals acid odor with the adsorption, and the copper treats acid odor with a chemical absorption without UV irradiation; Cu-mesoporous TiO_2 also exert the photocatalytic decontamination with UV irradition. 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 TiO_2

The synthesis process of mesoporous TiO_2 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 TiO_2 could be obtained. Cu-mesoporous TiO_2 was synthesized via the photoreduction method. Mesoporous TiO_2 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 TiO_2 could be obtained. The stoichiometric weight ratio of Cu and TiO_2 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 oder via Cu-mesoporous TiO_2 testing system

The removal efficiency of acid oder 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 midget 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 TiO_2, mesoporous TiO_2 and Cu-mesoporous TiO_2 were 33.24, 101.75 and 99.86 m^2/g, listed in Table I; The surface area of mesoporous TiO_2 was enhanced by added F127 template in the synthesis procedure, and the three times the value of TiO_2. Cu modification on mesoporous TiO_2 didn't decrease the surface area sufficiently due to the low dosage of 2wt% Cu for TiO_2. Each average pore size of photocatalyst was calculated from the Equation (1)

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

the pore volume of Cu-mesoporous TiO_2 didn't decrease with lowering surface area, thus the its average pore size is little larger than that of mesoporous TiO_2.

The crystalline structure of TiO_2, mesoporous TiO_2 and Cu-mesoporous TiO_2 measured by XRD, illustrated on Fig. 1.

The TiO_2 was characterized as the pure anatase phase, both mesoporous TiO_2 and Cu-mesoporous TiO_2 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]

$$X = \frac{1}{1 + 0.8(I_A/I_B)} \qquad (2)$$

Where IA is the integrated (101) intensity of anatse 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 TiO_2 and Cu-mesoporous TiO_2 were 27.6 and 27.8 %, respectively.
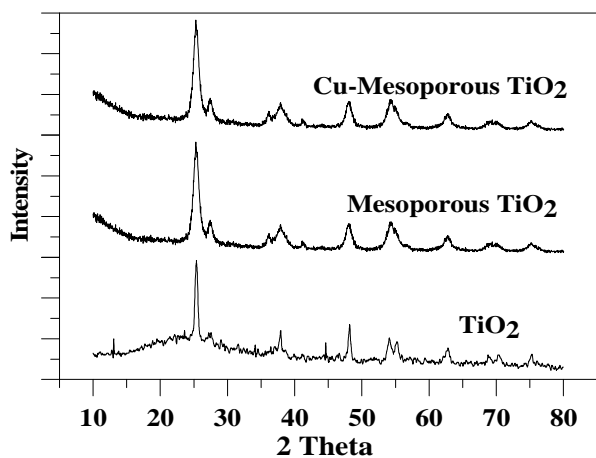

Fig. 1 XRD spectra of TiO_2, mesoporous TiO_2 and Cu-mesoporous TiO_2

This result indicated Cu modified on mesoporous TiO_2 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 TiO_2, mesoporous TiO_2 and Cu-mesoporous TiO_2 were 33.9, 18.6, and 18.8 nm. Cu modified on mesoporous TiO_2 via photoreduction process didn't also influence the crystallite size. The crystallite size of mesoporous TiO_2 was smaller than that TiO_2 might be contributed to the longer ageing period and self-assembly procedure between surfant and Ti source.

In Figure 2, the TEM image indicated that Cu-mesoporous TiO_2 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.
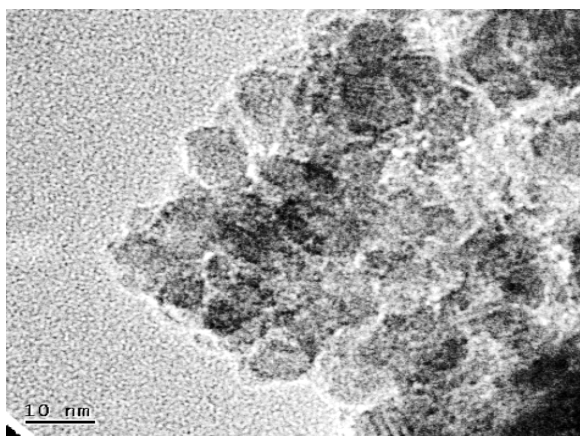

Fig. 2 TEM image of Cu-mesoporous TiO_2

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.
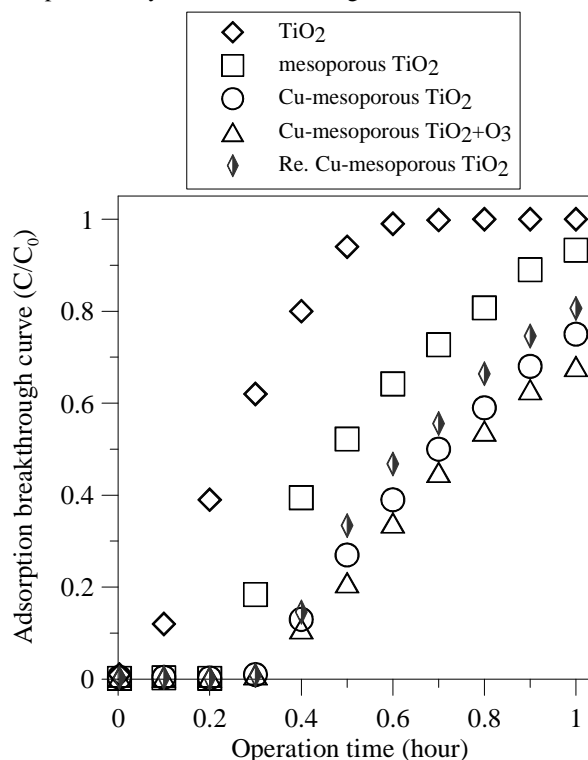

Fig. 3 Comparison the adsorption performance among each photocatalyst for acid odor

Operated on the 0.11m/s of linear velocity and 50ppm of acetic acid, the 0.1g TiO_2 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 TiO_2 was 3 times value of TiO_2, and then mesoporous TiO_2 showed the better adsorption ability. The adsorption efficiency of acid odor on mesoporous TiO_2 could maintain above 90% until 15min, the mesoporous TiO_2 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 TiO_2 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 TiO_2 was prolonged, and happened on 25min of operating time. Adsorping after 1hour, Cu-mesoporous TiO_2 still had the 30% removal efficiency for acid odor. The very little difference of material characteristics, listed in Table I, between mesoporous TiO_2 and Cu-mesoporous TiO_2 was deserves to be mentioned, the pore and crystal structure of mesoporous TiO_2 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 TiO_2 didn't block the surface area. Ozone assisting Cu-mesoporous TiO_2 for acid odor removal was also discussed in this study; however the adsorption efficiency of acid odor on Cu-mesoporous TiO_2 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 TiO_2 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 TiO_2; then infusing the other dry flow, lighting on the UV lamp and increasing temperature at $70^{o}C$, 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 TiO_2 under UV irradiating. Thus the removal ability of regenerated Cu-mesoporous TiO_2 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 TiO_2 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 TiO_2. Thus the photocatalysis ability of mesoporous TiO_2 could be improved and showed 5 times the degradation efficiency of TiO_2.

In addition, the better performance of mesoporous TiO_2 was also contributed to the 27.6% fraction of rutile phase, the appropriate ratio of rutile and anatase phase in TiO_2 was verified to profit the VOCs photodegradation [26].

The photodecomposition efficiency of pollutant on Cu-mesoporous TiO_2 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 photocatalyis process via Cu-mesoporous TiO_2 enhanced degradation efficiency to 60% distinctly, better than the single photocatalysis process. Under UV irradiation and photocatalysis via Cu-mesoporous TiO_2, free oxygen radical decomposed from ozone was accelerative and assisted the acid odor destroyed. The regeneration Cu-mesoporous TiO_2 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.
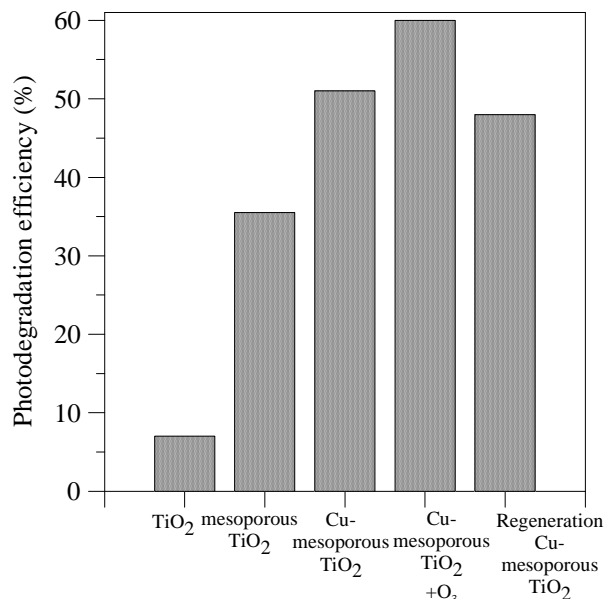

Fig. 4 Comparison the degradation performance among each photocatalyst for acid odor

IV. CONCLUSION

This study synthesized Cu-mesoporous TiO_2 to remove and degrade acid odor, acetic acid, which is usually detected in atmosphere of the science industries park. Without UV irradiation, TiO_2, mesoporous TiO_2 and Cu-mesoporous TiO_2 were compared for the odor removal via adsorption. Owing to dual mechanisms of adsorption and absorption, Cu-mesoporous TiO_2 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 TiO_2 still presented the more outstanding performance on degrading acid odor. The larger surface area and more porous characteristic of Cu-mesoporous TiO_2 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 TiO_2 also enhanced the performance more than TiO_2 in pure anatase phase. Ozone assistance could help Cu-mesoporous TiO_2 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 TiO_2, 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 TiO_2 , and furthermore help used Cu-mesoporous TiO_2 to maintain the fine photodegradtion efficiency of acid odor.

The removal performance of Cu-mesoporous TiO_2 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.

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