Photocatalytic degradation of gaseous trichloroethene using immobilized ZnO/SnO$_2$ coupled oxide in a flow-through photocatalytic reactor

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Abstract: The photocatalytic degradation of gaseous trichloroethene (TCE) was investigated on immobilized ZnO/SnO$_2$ coupled oxide in a flow-through photocatalytic reactor. It was found that gaseous photocatalysis is an efficient method for volatile organic compounds' abatement and air purification. Degradation of ~100% was found for TCE at the concentrations examined, up to 400 ppmv, in a flow-through dry synthetic gas stream. In our tested conditions, the flow rate had little influence on the photocatalytic degradation efficiencies of TCE, while the relative humidity had a significant influence on the photocatalytic degradation of TCE. The photocatalytic degradation efficiencies of TCE increased slowly below 20% relative humidity and then decreased as the relative humidity increased further. The deactivation of used immobilized photocatalyst was not observed within the 200 h testing period in the present experiment, although the surface of the photocatalyst changed greatly during the use of the photocatalyst.
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Keywords: gaseous photocatalysis; flow-through reactor; immobilized photocatalyst; coupled oxides; trichloroethene

INTRODUCTION

Volatile organic compounds (VOCs) are widely used in (and produced by) both industrial and domestic activities.[1] Among VOCs, volatile chlorinated organic compounds such as trichloroethene (TCE), tetrachloroethene (PCE) and dichloromethane (DCM) have been widely used as extracting solvents as well as degreasing and cleaning agents in industrial processes.[2,3] Volatile chlorinated organic compounds are some kind of the most commonly detected pollutants in hazardous waste sites and landfills in many countries.[4,5] Moreover, they are also very commonly detected in indoor air.[6] As a result, the widespread presence of volatile chlorinated organic compounds in the environment poses a serious challenge because most of these compounds are toxic, and some are considered to be carcinogenic, mutagenic, or teratogenic, and they are extremely persistent in the environment.[7]

Many countries have implemented VOC emission control measures. However, it is still a technical and management problem to reduce the emission of these hazardous air pollutants in industrial processes and remove them from polluted indoor or outdoor air. Thus, to remove volatile chlorinated organic compounds from the atmosphere is of great interest. Among the most commonly used methods, adsorption on activated carbon for emission control can only change the organic pollutants from one phase to another, and the absolute toxicity of the substances is still preserved.[8] However, photocatalytic oxidation using TiO$_2$ as a photocatalyst has been receiving increasing attention for VOC abatement and air purification, and has been demonstrated as an efficient abatement technology for the mineralization of these volatile chlorinated organic compounds.[9–12] Most gaseous photocatalysis studies are focused on the

degradation feasibility and reaction mechanism of photocatalysis on various forms of TiO_2, for example particulate TiO_2 and immobilized TiO_2 film, and little research has been carried out on the improvement in the gaseous photoactivity of the photocatalyst and the development of new photocatalysts for VOC abatement in gaseous photocatalysis. Several attempts have been made to improve the photocatalytic efficiency of titanium dioxide or develop new photocatalysts, such as noble metal deposition,[13] ion doping[14,15] and coupled metal oxides.[16] Many binary and ternary metal oxides have been reported to improve the photocatalytic degradation efficiency of organic pollutants in water. In our previous study,[17,18] a nano-sized coupled oxide, ZnO/SnO_2, was prepared using two simple co-precipitation methods, and it was successfully used to evaluate the photocatalytic oxidation enhancement of Methyl Orange in water. We now consider the photoactivity of our coupled oxide photocatalyst used for VOC abatement and air purification. To look for a photocatalyst or find a good method to regenerate the used photocatalyst, the photocatalytic degradation of a model VOC, TCE, was investigated using ZnO/SnO_2 coupled oxide photocatalyst immobilized on a porous nickel mesh.

EXPERIMENTAL
Materials
TCE (analytical grade) with purity over 99.8% was purchased from Sigma and used as supplied. Ultra-high-purity nitrogen and oxygen were supplied directly from gas cylinders. Nitrogen carrying 400 ppmv TCE was obtained by the evaporation of TCE using predetermined values of flow rate of carrier gas through a saturator containing TCE at the temperature of 40 °C.

Preparation and characterization of ZnO/SnO_2 coupled oxide immobilized photocatalyst
The nano-sized coupled oxide catalyst ZnO/SnO_2 (2:1) was prepared using the co-precipitation method and characterized as described previously.[17] Calcination at 600 °C for 10 h leads to SnO_2 and ZnO in the coupled oxide with mean sizes of about 3.9 nm and 46.4 nm, respectively. Five g of this powder was added into 10 cm³ deionized water, stirred for 30 min, then uniformly loaded onto a disc of porous nickel mesh (radius 4.5 cm). The loaded disc was dried at 110 °C for 2 h, and washed with deionized water three times, dried at 110 °C again for 1 h, then weighed for further usage. The net loaded weight of the catalyst is 4.81 g per disc. The immobilization was conducted at low temperature so that no change was expected in the chemical properties of the catalyst. The SEM images were obtained by a model LEO1530VP microscope (LEO, Germany). The surface morphologies of the porous nickel mesh coated with or without nano-sized coupled oxide are shown in Fig 1. Compared with the original nano-sized coupled oxide ZnO/SnO_2
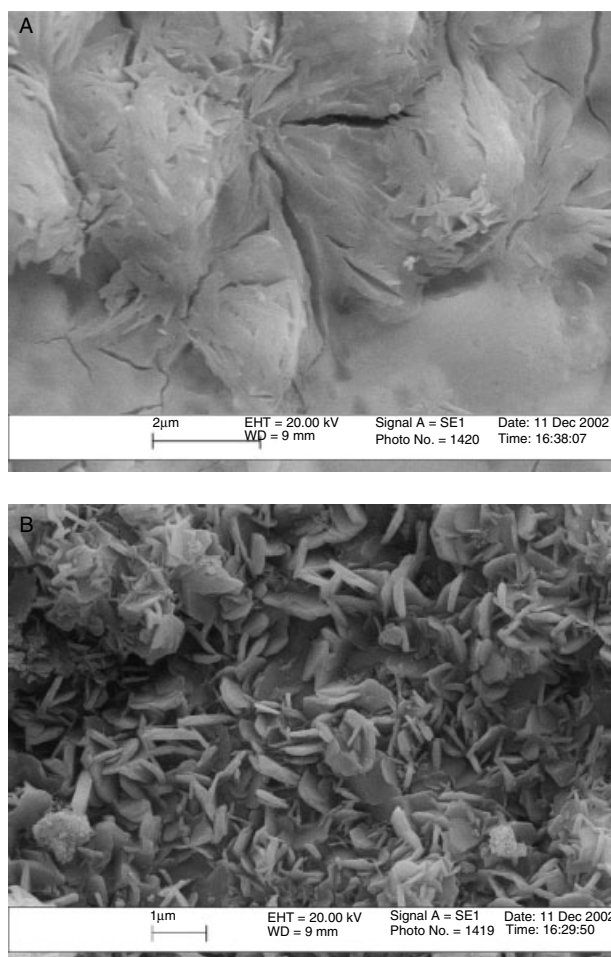

Figure 1. SEM images of: (A) porous nickel mesh substrate; (B) coupled oxides photocatalyst immobilized onto porous nickel mesh.

powder,[17] it can be seen from the figure that the immobilized coupled oxide particles on nickel mesh had an apparent aggregation and greater size. Moreover, the catalyst was distributed uniformly on the supported porous nickel mesh, and the substrate was completely covered by the catalyst. The phase did not change after the catalyst was immobilized onto the nickel mesh because the heat treatment temperature is only 110 °C. In the present work, the immobilized photocatalyst was repeatedly used for all experiments in order to investigate the reuse and deactivation of the photocatalyst.

Flow-through gaseous photocatalytic reactor
The flow-through photocatalytic reactor used for the gas–solid photocatalytic degradation of TCE is shown in Fig 2A. It consists of a 125 W high-pressure mercury lamp (GGZ125, Shanghai Yaming Lighting Co, Ltd) which was sleeved in a Pyrex glass tube located inside a stainless steel cylinder containing an immobilized photocatalyst disc. The reaction gas stream was composed of four gases (pure nitrogen, pure oxygen, humidified nitrogen, nitrogen contaminated with TCE), and the oxygen content was 20%. The schematic set-up of the gas flow systems is
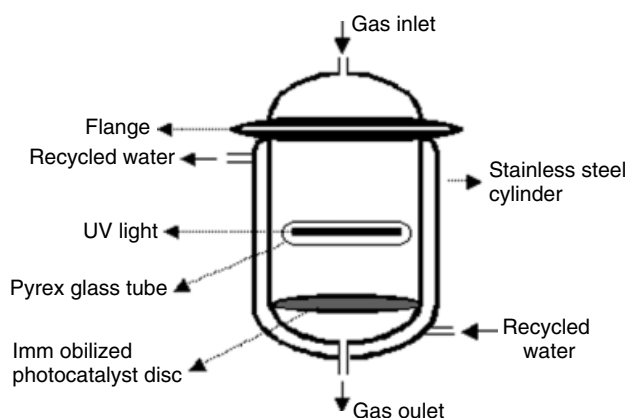
Figure 2A. Schematic diagram of a flow-through photocatalytic reactor.

shown in Fig 2B. When reaction started, the gas stream entered the stainless steel photocatalytic reactor from the top, passed through the reactor, reacted with the immobilized photocatalyst on the surface, and then exited from the bottom to an alkaline trap to assure the retention of any acidic products leaving the reaction vessel.

Procedure and analytical methods

Nitrogen gas containing TCE was prepared by carrying TCE vapour into an initially evacuated clean cylinder with a flow of pure nitrogen gas. Humidified nitrogen gas was prepared by bubbling nitrogen through a saturator containing deionized water at the temperature of 40 °C, and the relative humidity was adjusted by the flow rate of bubbling nitrogen and probed with a barothermohygrogram *in situ*. The gas mixture stream was forced to flow through the immobilized photocatalyst where TCE was degraded. In a typical test, the gas mixture stream with TCE passed through the photocatalytic reactor in the absence of illumination until the gas–solid adsorption

equilibrium was established under a constant flow rate. Photocatalytic degradation was started by switching on the UV lamp. Except as indicated, the flow rate of the gas mixture was $300 \, cm^3 \, min^{-1}$ with an initial TCE concentration of 400 ppmv. All gaseous degradation reactions were conducted under an atmosphere without water vapour except for the experiments on the effect of water vapour.

The effluent from the photocatalytic reactor was sampled with a $50 \, mm^3$ gas-tight syringe and analysed in an HP 6890 gas chromatograph (GC) equipped with an electron capture detector (ECD). The photocatalytic degradation efficiency of TCE was defined as $(1 - C/C_0) \times 100$, where C_0 and C are respectively the concentrations of TCE in the feed to and effluent from the reactor. Ultra-high-purity nitrogen was used as carrier gas, and the GC column was a HP-5 capillary column ($50 \, m \times 0.32 \, mm \times 0.25 \, \mu m$) with a flow of $2.0 \, cm^3 \, min^{-1}$. The GC oven temperature was programmed to be initially at 40 °C for 2 min, then raised to 80 °C at a rate of 2 °C min^{-1} and held for 2 min, and then to 230 °C at a rate of 15 °C min^{-1} and held for 2 min. The detector and injector temperatures were 250 °C and 190 °C respectively, and the gas volume injected was $5 \, mm^3$.

RESULTS AND DISCUSSION
Adsorption of TCE onto immobilized photocatalyst

The adsorption of pollutants onto the photocatalyst surface is the first step of the photocatalytic reaction; moreover, the adsorbability of the pollutants onto the photocatalyst surface is an important factor to evaluate the efficiency of the photocatalytic degradation of pollutants.[19] In the present work the adsorption of TCE at various relative humidities has been performed in the dark in the presence of the immobilized photocatalyst. The feed mixture flowed through the
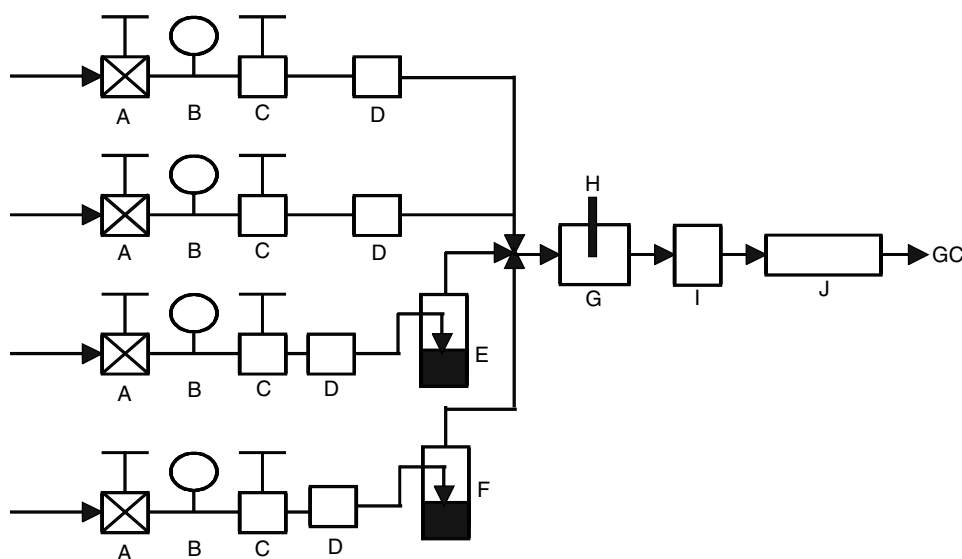

Figure 2B. Schematic set-up of the synthetic-gas flow and mixture systems. A: Pressure controller; B: pressure meter; C: flow controller; D: flow meter; E: TCE saturator; F: water vapour saturator; G: mixture system; H: humidity sensor; I: flow meter; J: photoreactor.
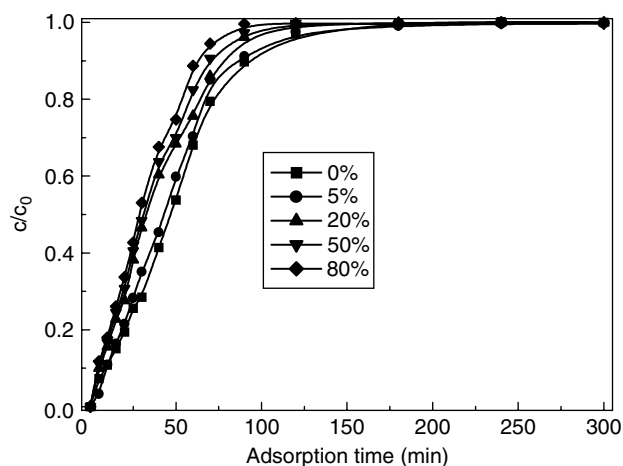
Figure 3A. Adsorption kinetics of TCE onto immobilized photocatalyst at various relative humidities.
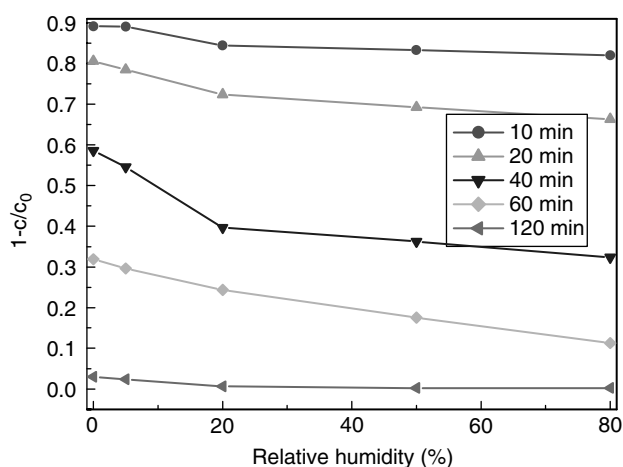

Figure 3B. Dependence on relative humidity of amount of TCE adsorbed.

immobilized photocatalyst for a certain time until a steady exit concentration of TCE was achieved. The adsorption in the dark was performed under an identical constant flow with the concentration of TCE at 400 ppmv, and the adsorption kinetics profiles at various relative humidity are given in Fig 3A, which shows that the adsorption equilibrium of TCE in the absence of water vapour can be completely established within 2 h. Moreover, it was found that the relative humidity had a slight effect on the adsorption kinetics of TCE. In order to clearly see the relationship between the relative humidity and amount of TCE adsorbed, the effect of relative humidity on the adsorption of TCE on the surface of photocatalyst was also investigated, and the profiles are plotted in Fig 3B. From this figure, we can find that at any tested interval an inverse dependence of relative humidity on the adsorbed amounts of TCE was obtained, ie with increase in the relative humidity, the adsorption of TCE on photocatalyst decreased slowly at any reaction interval. This indicated that TCE had a lower adsorption affinity than water, and there was a strong competitive adsorption with

water molecules at higher humidity. The higher the relative humidity is, the less TCE is adsorbed onto the immobilized photocatalyst, and the sooner the adsorption equilibrium is achieved. No TCE degradation was found when gas mixture streams were passed through the immobilized photocatalyst in the absence of light. All photocatalytic degradation experiments in the present work were conducted after the adsorption equilibrium of TCE was established.

Photocatalytic degradation of TCE

It has been reported that in the absence of photocatalyst, the photolysis of TCE was not apparent under illumination provided only by a high-pressure mercury lamp. This indicated that TCE could not be decomposed directly by UV light of 365 nm, presumably because the maximum adsorption wavelength of TCE was about 240 nm.[20] In the present work, a high-pressure mercury lamp emitting radiation at a maximum wavelength of 365 nm was also used to conduct the photocatalytic reaction of TCE, thus the photodegradation of TCE without photocatalyst should be investigated first. Both photodegradation and photocatalytic kinetics curves of TCE are shown in Fig 4A. It was found that in absence of photocatalyst TCE was degraded partially when irradiated by UV light, and the photolytic efficiency obtained was only 14%. This is because with increasing the reaction time, the photochemical degradation reaction reached a photochemical steady-state, ie the photochemical reaction efficiency reaches a maximum of 14% in the continuous flow reaction stream within a few minutes of the start. However, in the presence of ZnO/SnO_2 immobilized photocatalyst, the TCE concentration in the reactor decreased strongly, indicating an apparent photocatalytic degradation of TCE when the UV light was turned on. In this case, the photocatalytic degradation efficiency of TCE was as high as $\sim$100% under the experimental set-up and the conditions described above.

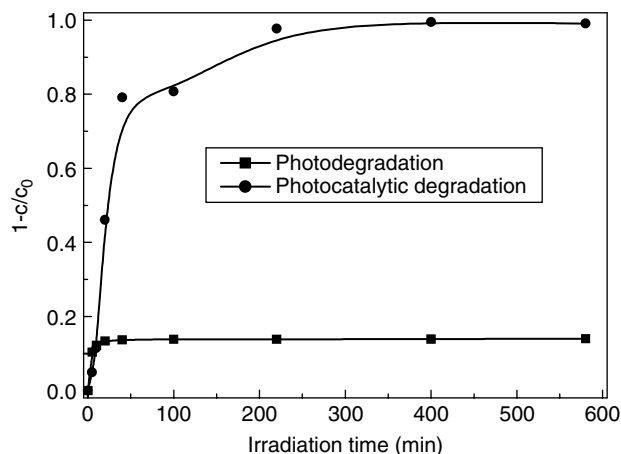In order to completely understand the effect of UV light, the photocatalytic experiments were carried

Figure 4A. Photocatalytic degradation and photodegradation kinetics of TCE.
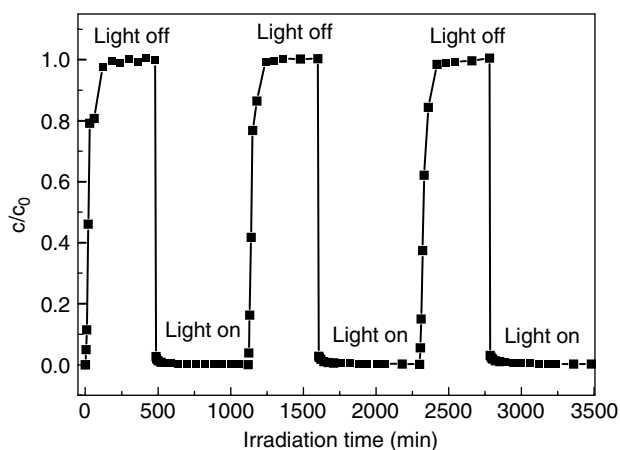
Figure 4B. Light on–off experiments on photocatalytic degradation of TCE.

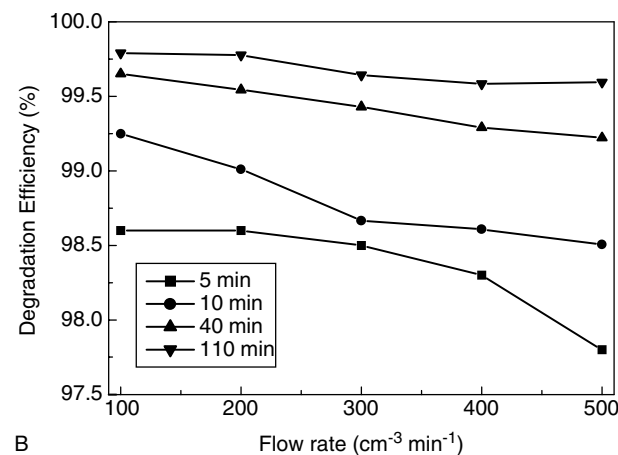**Figure 5.** Effect of flow rate on TCE conversion efficiency.

out without UV light initially, then the UV light was switched on and off several times. The results are shown in Fig 4B. From this figure, it is noted that under the general conditions, by turning off the UV light, the concentration of TCE will be kept constant after 2 h adsorption. The results indicated that the photocatalyst alone could not decompose TCE without UV light. However, when the UV light was turned on, the concentration of TCE dropped dramatically and reached the steady state within 110 min. On the contrary, the TCE concentration was raised to the original concentration within 120 min when the UV light was turned off. It was found that the concentration of TCE did not decrease until the UV light was turned on again, then the decomposition reaction occurred with the same pattern as the previous one, ie reaching the steady state again. The light off–on procedures were repeated and the results were the same as the previous ones. This indicated that the UV light played an important role in the photocatalytic degradation of gaseous TCE.

The effect of flow rate

In heterogeneous catalysis, the factors for the rate-controlling step are mass transfer and surface reaction control.[20,21] At low flow rates, the reaction rate is under the influence of mass transfer, for which the increase of flow rate increases the reaction rate. The mass transfer effect from the bulk phase to the surface increases with the flow rate, and then gradually levels off. The variation of reaction efficiencies of TCE degradation in the flow rates ranging from $100 \, cm^3 \, min^{-1}$ to $500 \, cm^3 \, min^{-1}$ are shown in Fig 5(A). From this figure, it is found that the photocatalytic degradation efficiencies decreased slowly for the first 10 min, then levelled off and had the same trend thereafter with increase of the flow rate. The photocatalytic degradation efficiencies at various reaction time under different flow rates are shown in Fig 5(B), it was found that the flow rate had a slight effect on the photocatalytic degradation efficiencies of TCE. For example, the degradation
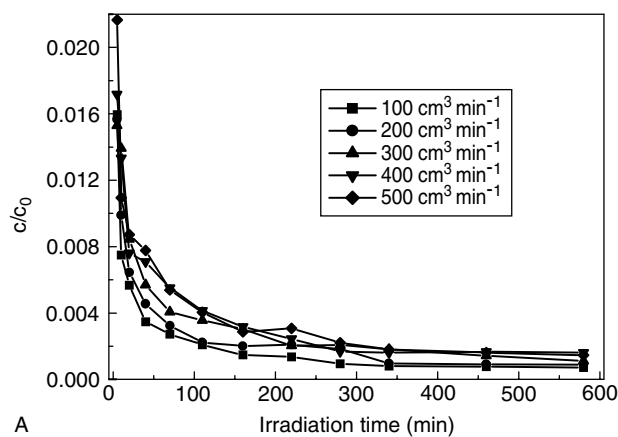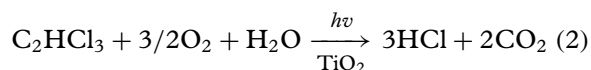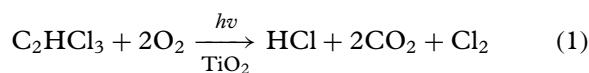
efficiencies in the first 5 min under various flow rates were 98.6%, 98.6%, 98.5%, 98.3% and 97.8%, respectively. Moreover, as the reaction time increased the influence of flow rate on the photocatalytic efficiency became less and less. The degradation efficiencies at the photosteady state varied very little under various flow rates. Thus, we could conclude that there was no apparent mass transfer control effect and the flow rate had little influence on the photocatalytic degradation of TCE in this work. Thus, in the present investigation, the flow rate of $300 \, cm^3 \, min^{-1}$ was selected for other studies.

The effect of relative humidity

In the above experiments, TCE degradation reactions were all conducted under an atmosphere without water vapour. However, water vapour plays an important role in the photocatalytic degradation of gaseous VOCs. Many researchers have investigated the photocatalytic degradation of TCE using TiO_2 as photocatalyst in the presence or absence of water vapour.[10,12,22,23] Huang and Mariñas found that TCE degradation was not affected by relative humidity up to 20%, but it deteriorated as the gas mixture approached saturation with respect to water vapour.[23] But Amama et al believed that the presence of water vapour molecules suppressed or delayed the Cl atom-propagated chain reaction.[22]

To date, there is controversy relating to the effect of water vapour on photocatalytic degradation of TCE. Huang and Mariñas pointed out that in the absence of water vapour, TCE degradation at high oxygen concentrations, including that of ambient air resulted in the formation of inorganic compounds, with hydrochloric acid and molecular chlorine being the primary chlorine-containing products.[23] Both Liu *et al*[24] and Nimbles *et al*[25] also found that CO_2, HCl and Cl_2 were detected as the final products, and a stoichiometric formula was given (see eqn (1)). However, Dibble and Raupp reported that CO_2 and HCl were the final products of the photocatalytic oxidation of TCE when water vapour was incorporated in the reactant stream,[26] and Amama *et al* presented a stoichiometric chemical equation of TCE photocatalysis in the presence of water vapour (eqn (2)).[22]

$$C_2HCl_3 + 2O_2 \xrightarrow[\text{TiO}_2]{hv} HCl + 2CO_2 + Cl_2 \qquad (1)$$

$$C_2HCl_3 + 3/2 O_2 + H_2O \xrightarrow[\text{TiO}_2]{hv} 3HCl + 2CO_2 \qquad (2)$$

Comparing eqn (1) with eqn (2) we can easily see that the gaseous TCE can be degraded with or without water vapour. However, what is the underlying reason for the effect of water vapour on the photocatalytic degradation of TCE? Thus, we conducted the photocatalytic degradation experiments of TCE in the range of relative humidity from 0% to 80%, and the results are shown in Fig 6(A). It was found that relative humidity had a significant influence on the photocatalytic degradation efficiencies of TCE, especially for the first 5 min. The dependence on relative humidity of the degradation efficiency of TCE in various reaction times is shown in Fig 6(B). From this figure we can see that at any time interval, the photocatalytic degradation efficiency for TCE increased slowly at up to 20% relative humidity and then decreased substantially with further increase in the relative humidity, and the photocatalytic conversion of TCE was significantly inhibited by excessive water vapour. About 99.2% TCE was degraded at 0% relative humidity, while at 20% relative humidity, about 99.8% TCE conversion was achieved at steady state. But only 96.4% and 92.9% of TCE was degraded at 50% and 80% relative humidity, respectively. The results revealed that a little water vapour could promote the photocatalytic degradation of TCE, while excessive water vapour could inhibit the photocatalytic degradation of TCE. This phenomenon is in agreement with to the observations reported previously.[23] The decrease in the photocatalytic degradation efficiencies was probably due to the increase in water vapour competing with the adsorption sites on the photocatalyst's surface. Moreover, the decrease in the amounts of TCE initially absorbed on
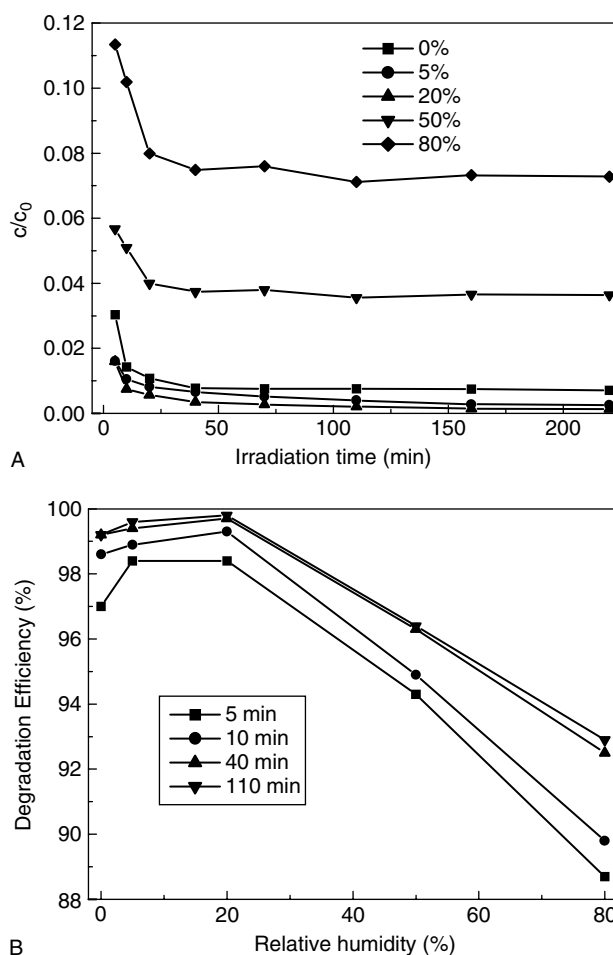

Figure 6. Effect of relative humidity on TCE conversion efficiency.

the photocatalyst with increase in the relative humidity may be another convincing reason accounting for the decrease of photocatalytic degradation efficiency at higher relative humidity.

Long-term photocatalytic activity of immobilized coupled oxide

It had been reported by many researchers that the photocatalytic activity of TiO_2 decreases dramatically after only a few minutes irradiation in the absence of water vapour; however, under an abundance of water vapour, the photocatalytic activity could be maintained indefinitely.[27,28] In this study, it was found that the photocatalytic degradation of gaseous TCE without water could be completely accomplished under our experimental conditions, and ~100% degradation was achieved for TCE concentrations examined up to 400 ppmv whilst the humidified atmosphere had a significant inhibiting effect on the photocatalytic degradation of TCE. Figure 7 presents the long-term photocatalytic degradation profiles. The lifetime experiments of immobilized photocatalyst were carried out with a flow rate of $300 \, \text{cm}^3 \, \text{min}^{-1}$ and without water vapour. It showed that when light was turned on the photocatalytic degradation efficiencies of TCE increased dramatically until it reached a steady state. Fortunately, the deactivation of used immobilized photocatalyst was not observed within
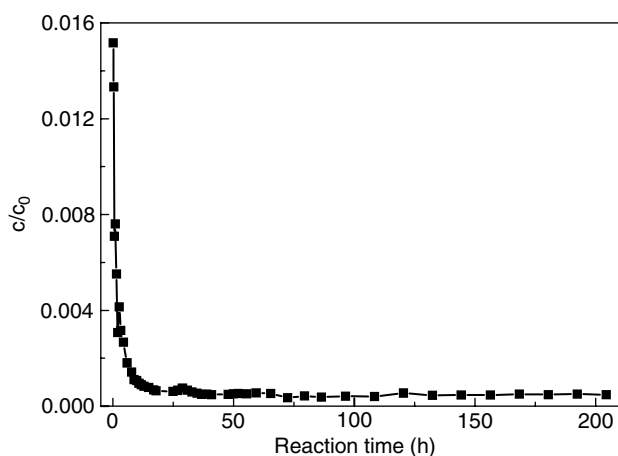
Figure 7. Effect of reaction time on photocatalytic activity of immobilized photocatalyst.

Figure 8. SEM images of used immobilized photocatalyst after: (A) about 100 h; (B) about 200 h.

our 200 h testing period. From the figure, we can easily see that the photocatalytic degradation efficiency of TCE remained nearly 100% after the immobilized photocatalyst had been used for 200 h. As a result, the gas-phase photocatalytic oxidation may be free of catalyst regeneration in this work. But this conclusion did not conform to the results reported in the literature.[27] This difference may be interpreted by the fact that the used immobilized coupled oxide photocatalyst could make charge separation more efficient than did TiO_2, thus decreasing the recombination of electrons and holes in the ZnO/SnO_2 couple.[17]

In order to further understand the deactivation and the surface morphology change, the used photocatalysts were also observed by SEM. The SEM micrographs of the immobilized photocatalyst used for 100 h and 200 h are presented in Fig 8(A and B, respectively). From this figure we can conclude that though the decrease in the photocatalytic degradation efficiencies for 400 ppmv TCE and the photocatalyst deactivation were not found within our 200 h testing time, the surface morphology of the photocatalyst was greatly changed. It was found that the surface of our immobilized photocatalyst was covered by a lot of colloid species, and the colloid species also accumulated with increase in the reaction time. The surface morphology change of the photocatalyst could be attributed to the long-term corrosion effect of HCl formed in the reaction. Thus, we can predict that the deactivation of immobilized photocatalyst will be observed with further usage. Thus, it is very necessary to develop a good photocatalyst regeneration method in further gaseous photocatalytic research.

CONCLUSIONS
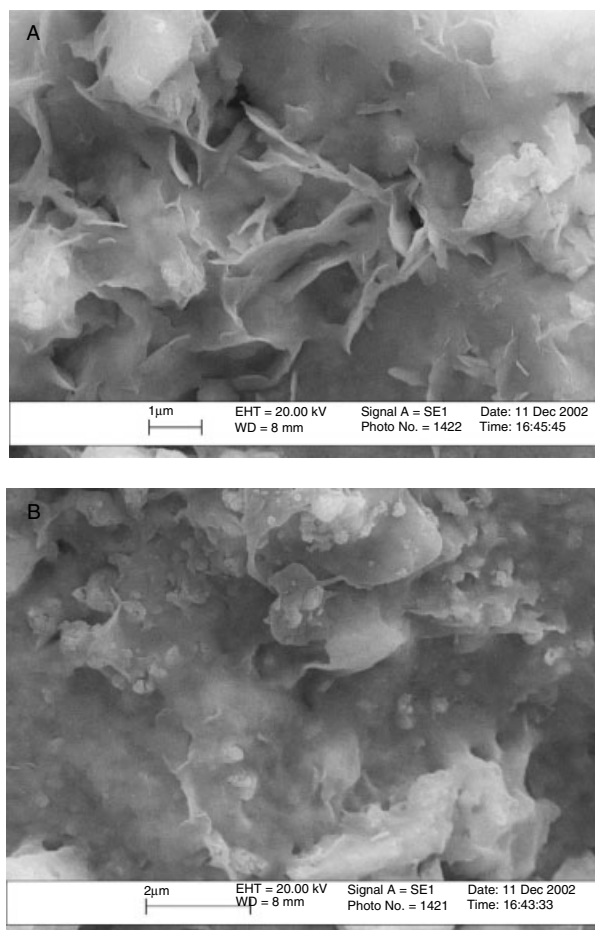(1) Gas−solid photocatalytic degradation is an efficient method for volatile chlorinated organic compounds' abatement and air purification using immobilized ZnO/SnO_2 coupled oxide as a photocatalyst.
(2) In our tested conditions, the flow rate had little influence on the photocatalytic degradation efficiencies of TCE, while the relative humidity had a significant influence on the photocatalytic degradation of TCE.
(3) No deactivation of the immobilized photocatalyst was observed within the 200 h testing period, and the gas-phase photocatalytic oxidation may be free of catalyst regeneration in this work.

REFERENCES
1 Wolf K, Yazdani A and Yates P, Chlorinated solvents—will the alternatives be safer. *J Air & Waste Manag Asso* **41**:1055−1066 (1991).

2 Kochany J and Bolton JB, Mechanism of photodegradation of aqueous organic pollutants. 2. Measurement of the primary rate constants for reaction of hydroxyl radicals with benzene and some halobenzenes using an EPR spin-trapping method following the photolysis of hydrogen peroxide. *Environ Sci Technol* **26**:262–265 (1992).

3 Purden AL and Ollis DF, Degradation of chloroform by photoassisted heterogeneous catalysis in dilute aqueous suspensions of titanium dioxide. *Environ Sci Technol* **17**:628–631 (1983).

4 Shen TT, Schmiidt CE and Card TR, *Assessment and Control of VOCs Emission from Waste Treatment and Disposal Facilities.* Van Nostrand Reinhold, New York (1993).

5 Zou SC, Lee SC, Chan CY, Ho KF, Wang XM, Chan LY and Zhang ZX, Characterization of ambient volatile organic compounds at a landfill site in Guangzhou, South China. *Chemosphere* **51**:1015–1022 (2003).

6 Hines AL, Grosh TK, Loyalka SK and Warder RC, *Indoor Air Quality and Control.* PTR Prentice Hall, Englewood Cliffs, NJ (1993).

7 Wilkinson CF, Being more realistic about chemical carcinogenesis. *Environ Sci Technol* **21**:843–850 (1987).

8 Hager S, Bauer R and Kudielka G, Photocatalytic oxidation of gaseous chlorinated organics over titanium dioxide. *Chemosphere* **41**:1219–1225 (2000).

9 Ao CH, Lee SC and Yu JC, Photocatalyst TiO_2 supported on glass fiber for indoor air purification: effect of NO on the photodegradation of CO and NO_2. *J Photochem Photobiol A: Chem* **156**:171–177 (2003).

10 Huang CH and Marińas BJ, Role of chlorine and oxygen in the photocatalytic degradation of trichloroethene vapor on TiO_2 films. *Environ Sci Technol* **31**:562–568 (1997).

11 Ollis DF, Photocatalytic purification and remediation of contaminated air and water. *Surface Chemistry and Catalytics/Chemie Des Surfaces et Catalyse* **3**:405–411 (2000).

12 Sánchez B, Cardona AI, Romero M, Avila P and Bahamonde A, Influence of temperature on gas-phase photoassisted mineralization of TCE using tubular and monolithic catalysts. *Catal Today* **54**:369–377 (1999).

13 Takeda K and Fujiwara K, Characteristics on the determination of dissolved organic nitrogen compounds in natural waters using titanium dioxide and platinized titanium dioxide mediated photocatalytic degradation. *Wat Res* **30**:323–330 (1996).

14 Choi W, Termin A and Hoffmann MR, The role of metal ion dopants in quantum-sized TiO_2: correlation between photoreactivity and charge carrier recombination dynamics. *J Phys Chem* **98**:13 669–13 679 (1994).

15 Yu JC, Zhang L, Zheng Z and Zhao J, Synthesis and characterization of phosphated mesoporous titanium dioxide with high photocatalytic activity. *Chem Mat* **15**:2280–2286 (2003).

16 Li XZ, Li FB, Yang CL and Ge WK, Photocatalytic activity of $WO_x–TiO_2$ under visible light irradation. *J Photochem Photobiol A: Chem* **141**:209–217 (2001).

17 Wang C, Zhao JC, Wang XM, Mai BX, Sheng GY, Peng PA and Fu JM, Preparation, characterization and photocatalytic activity of nano-$ZnO_2–SnO_2$ coupled photocatalyst. *Appl Catal B: Environ* **39**:843–848 (2002).

18 Zhang ML, An TC, Hu XH, Wang C, Sheng GY and Fu JM, Preparation and photocatalytic properties of a nanometer $ZnO–SnO_2$ couple oxide. *Appl Catal A: General* **260**:215–222 (2004).

19 Lu MC, Photocatalytic oxidation of propoxur insecticide with titanium dioxide supported on activated carbon. *J Environ Sci Health* **B34**:207–223 (1999).

20 Wang KH, Tsai HH and Hsieh YH, A study of photocatalytic degradation of trichloroethylene in vapor phase on TiO_2 photocatalyst. *Chemosphere* **36**:2763–2773 (1998).

21 Levenspiel O, *Chemical Reaction Engineering*, 2nd edn., John Wiley & Sons, New York (1972).

22 Amama PB, Itoh K and Murabayashi M, Photocatalytic oxidation of trichloroethene in humidified atmosphere. *J Molec Catal A: Chem* **176**:165–172 (2001).

23 Huang CH and Marińas BJ, Role of water in the photocatalytic degradation of trichoroethylene vapor on TiO_2 films. *Environ Sci Technol* **31**:1440–1445 (1997).

24 Liu H, Cheng SA, Zhang JQ, Cao CN and Jiang WC, The gas-photocatalytic degradation of trichloroethylene without water. *Chemosphere* **35**:2881–2889 (1997).

25 Nimbles MR, Jacoby WA, Blake DM and Milne TA, Direct mass spectrometric studies of the destruction of hazardous wastes. *Environ Sci Technol* **27**:732–740 (1993).

26 Dibble LA and Raupp GB, Fluidized-bed photocatalytic oxidation of trichloroethylene in contaminated air streams. *Environ Sci Technol* **26**:492–495 (1992).

27 Raupp GB and Junio TC, Photocatalytic oxidation of oxygenated air toxics. *Appl Surface Sci* **72**:321–327 (1993).

28 Dibble LA and Raupp GB, Kinetics of the gas-solid heterogeneous photocatalytic oxidation of trichloroethylene by near UV illuminated titanium dioxide. *Catal Lett* **4**:345–354 (1990).