

## Compact and effective photocatalytic air-purification unit by using of mercury-free excimer lamps with TiO<sub>2</sub> coated titanium mesh filter

Tsuyoshi Ochiai,<sup>\*ab</sup> Yasuji Niitsu,<sup>c</sup> Go Kobayashi,<sup>c</sup> Masahiro Kurano,<sup>c</sup> Izumi Serizawa,<sup>c</sup> Koji Horio,<sup>d</sup> Kazuya Nakata,<sup>ab</sup> Taketoshi Murakami,<sup>a</sup> Yuko Morito<sup>bd</sup> and Akira Fujishima<sup>ab</sup>

Received 13th July 2011, Accepted 29th July 2011

DOI: 10.1039/c1cy00270h

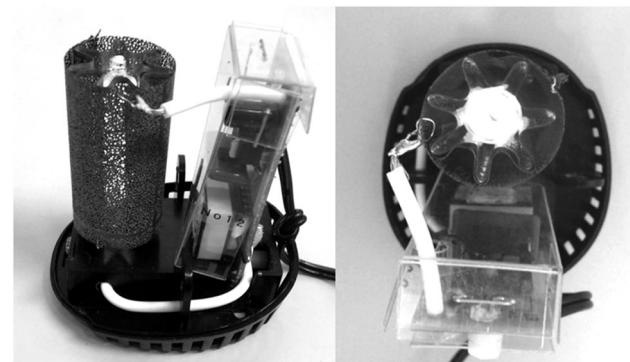
**A photocatalyst–excimer–lamp hybrid reactor was investigated using a mercury-free xenon chloride excimer lamp wrapped with a TiO<sub>2</sub> modified titanium-mesh sheet (TMiP). Significant decomposition of 6 ppm of methylmercaptane gas has been achieved by the reactor in a 36 L box within 3 h.**

Since the discovery of photocatalytic water splitting by TiO<sub>2</sub> in 1967, the strong oxidation ability of TiO<sub>2</sub> has received growing attention.<sup>1–3</sup> TiO<sub>2</sub> generates hydroxyl radicals and superoxide ions by UV light irradiation. These are highly reactive with organic compounds. Recently, environmental contamination has become a serious problem in the world. Thus, the strong oxidation ability of TiO<sub>2</sub> is expected to resolve these problems. However, there are several limitations such as electron–hole recombination, low efficiency, and difficulty in decomposition of large amounts of pollutants. Moreover, use of mercury lamps, a typical UV-source for photocatalysis, should be avoided due to their environmental risk. Therefore, effective photocatalysis technology with a mercury-free UV-source is required. In the present work, a novel air-purification reactor was investigated by using an excimer lamp with a TiO<sub>2</sub> modified titanium-mesh sheet (TMiP<sup>TM</sup>).<sup>4</sup> TMiP provides excellent air pass through while maintaining a high level of surface contact. A xenon chloride excimer lamp generates 308 nm of UV light with high intensity and a large irradiation area. An important point is that TMiP in the reactor is used not only as a photocatalyst but also as one of the electrode of excimer lamp for generation of dielectric barrier discharge (outer electrode in Fig. 2). This structure makes sure of efficient UV irradiation onto the photocatalyst surface. The air purification efficiency of the reactor was examined by a high concentration methylmercaptane (CH<sub>3</sub>SH) decomposition test.

An overview and a schematic view of the photocatalyst–excimer–lamp hybrid reactor are shown in Fig. 1 and 2,

respectively. A xenon chloride filled quartz tube (10 mm i.d. × 55 mm length) was wrapped in a corrugated TMiP sheet. The fabrication method of TMiP was previously reported.<sup>4</sup> The SEM image of TMiP is shown in the graphical abstract. The induction electrode is embedded in the quartz tube and the discharge electrode is a TMiP sheet connected to ground. A commercial electric power line of 50 Hz and 100 V was connected through a power supply. We used a voltage of 8 kVp-p, a frequency of 50 kHz, and a power of 5 W. When the AC high voltage is applied between the two electrodes, a dielectric barrier discharge occurs in the quartz tube which provided intense narrow band radiation at 308 nm from xenon chloride (XeCl\*).<sup>5</sup> UV intensity was measured using a UV RADIO METER UV-M03A with a UV-SN31 sensor head (ORC Manufacturing).

A schematic diagram of a total experimental system used for CH<sub>3</sub>SH decomposition is shown in Fig. 3. The photocatalyst–excimer–lamp hybrid reactor and fan placed inside the test box (acryl sealed 36 L box). Air was blown on the reactor continuously. For continuous conditions, CH<sub>3</sub>SH gas was introduced into the box by a heated permeation tube-based gas standards generator (Gastec Co., Ltd.) and was exhausted after the reaction. For batch conditions, CH<sub>3</sub>SH gas flow was stopped at the concentration of 6 ppm. Time course of the concentration of CH<sub>3</sub>SH was measured by a Kitagawa's detector tube (Komyo Rikagaku Kogyo K.K.). The experiments were carried out at room temperature and atmospheric pressure. After decomposition testing, TMiP was washed with MilliQ



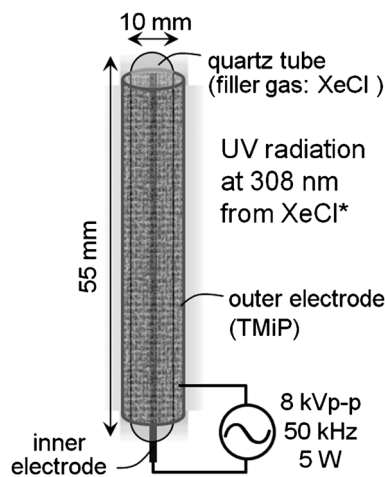
**Fig. 1** A side view (left) and a top view (right) of photocatalyst–excimer–lamp hybrid air-purification unit.

<sup>a</sup> Kanagawa Academy of Science and Technology, KSP East 421, 3-2-1 Sakado, Takatsu-ku, Kawasaki, Kanagawa, 213-0012, Japan. E-mail: pg-ochiai@newkast.or.jp; Fax: + 81-44-819-2070; Tel: + 81-44-819-2040

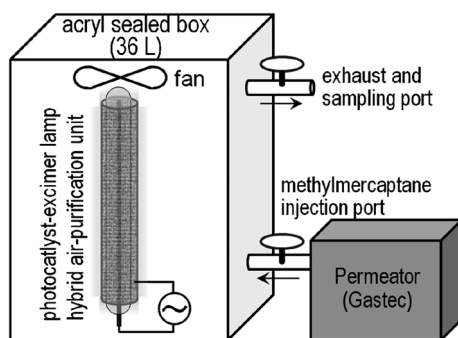
<sup>b</sup> Division of Photocatalyst for Energy and Environment, Research Institute for Science and Technology, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan

<sup>c</sup> ORC Manufacturing Co., Ltd., 3-9-6 Oyamagaoka, Machida, Tokyo 194-0295, Japan

<sup>d</sup> U-VIX Corporation, 2-14-8 Midorigaoka, Meguro-ku, Tokyo 152-0034, Japan



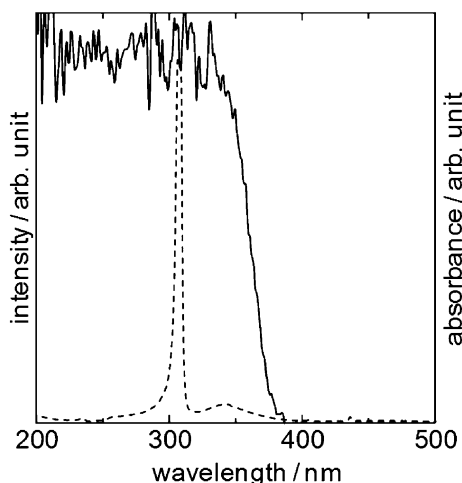
**Fig. 2** A schematic view of photocatalyst-excimer-lamp hybrid air-purification unit.



**Fig. 3** Schematic illustration of methylmercaptane decomposition test.

water for analysis of the decomposition products. An ion-chromatograph system (DX-120, DIONEX) with a separation column (IonPak AS12A, 4.0 mm i.d., 200 mm length, DIONEX) and a conductivity detector with a suppressor device (ASRS300, DIONEX) was used for the analysis.

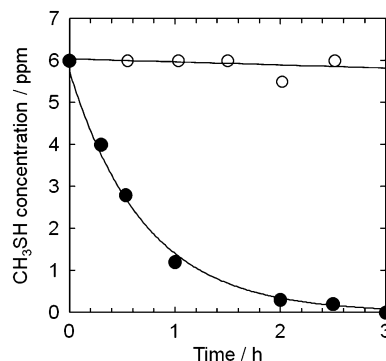
Fig. 4 shows the wavelength distribution for the emission from the excimer lamp and the absorptions of TMiP. Under the



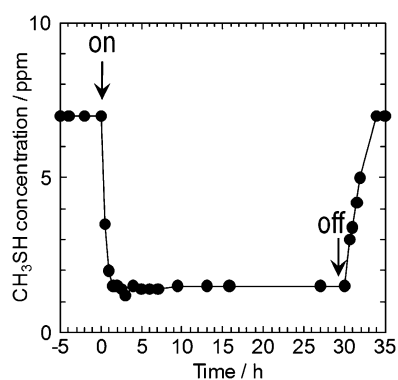
**Fig. 4** Wavelength distribution for the emission from the excimer lamp (dashed line) and the absorptions of TMiP (solid line).

present conditions, the excimer lamp emitted mainly 308 nm light (Fig. 4, dashed line) originating from  $\text{XeCl}^*$ .<sup>6,7</sup> The intensity of the UV light passed through the TMiP was  $0.5 \text{ mW cm}^{-2}$ . On the other hand, due to the wide band-gap of anatase  $\text{TiO}_2$  photocatalysts (3.2 eV), TMiP mainly absorbs ultraviolet photons with a wavelength of less than 387 nm (Fig. 4, solid line).<sup>3</sup> Therefore, emissions from the excimer lamp are in the range of the band gap of the  $\text{TiO}_2$  catalyst on the TMiP surface. Moreover, TMiP did not show any destruction during use as an electrode and UV irradiation. This result indicates the strong adhesion of  $\text{TiO}_2$  nanoparticles onto the TMiP surface.

Fig. 5 shows the time course of  $\text{CH}_3\text{SH}$  concentration in the test box under batch conditions. Under these conditions with the reactor turned off (open circles), the concentration was almost unchanged for 3 h. On the other hand, it can be seen that  $\text{CH}_3\text{SH}$  gas can be completely degraded within 3 h with the reactor turned on. The  $\text{CH}_3\text{SH}$  concentrations can be fitted with a pseudo-first-order kinetics given by the following equation,  $C = C_0 \exp(-k_1 t)$ . Where  $C_0$  is the initial  $\text{CH}_3\text{SH}$  concentration and  $k_1$  is the observed rate constant. The values of the  $k_1$  were calculated by exponential fitting of Fig. 5 to  $1.4 \text{ h}^{-1}$ . When the  $\text{TiO}_2$  is irradiated with UV light from the excimer lamp, excitation of electrons into the conduction band takes place, resulting in formation of holes in the valance band. Both the holes and the electrons migrate to the  $\text{TiO}_2$  surface, where they either recombine or react with adsorbed species such as  $\text{H}_2\text{O}$  and  $\text{O}_2$ . The holes oxidize adsorbed  $\text{H}_2\text{O}$  to  $\cdot\text{OH}$ , which are the potential oxidants in photocatalysis, whereas the electrons reduce  $\text{O}_2$  to  $\text{O}_2^{\cdot-}$ .<sup>3</sup>  $\text{CH}_3\text{SH}$  could be decomposed to  $\text{CO}_2$  and  $\text{SO}_4^{2-}$  by many possible pathways.<sup>8</sup> In the present conditions,  $8.2 \text{ mg L}^{-1}$  of  $\text{SO}_4^{2-}$  was detected in washing solution of TMiP after the decomposition test. Six ppm of  $\text{CH}_3\text{SH}$  in 36 L box could be converted to  $8.5 \text{ mg L}^{-1}$  of  $\text{SO}_4^{2-}$ . Therefore,  $\text{CH}_3\text{SH}$  was almost totally decomposed by the photocatalyst-excimer-lamp hybrid reactor. Interestingly, although it is thought that the fixation of  $\text{SO}_4^{2-}$  onto the  $\text{TiO}_2$  surface will eventually affect the performance of the photocatalysis, the  $\text{CH}_3\text{SH}$  decomposition test under continuous conditions at 7 ppm showed that the photocatalyst-excimer-lamp hybrid reactor prevented the increase of the  $\text{CH}_3\text{SH}$  concentration for 30 h (Fig. 6). In the present study, the relative surface area of TMiP was



**Fig. 5** Time course of  $\text{CH}_3\text{SH}$  concentration with the photocatalyst-excimer-lamp hybrid reactor turned off (open circles) and turned on (solid circles) in test box under batch condition.



**Fig. 6** Time course of CH<sub>3</sub>SH concentration under continuous condition.

664 cm<sup>2</sup> cm<sup>-2</sup> (real surface area/mathematical surface area). Therefore, the photocatalyst–excimer–lamp hybrid reactor could decompose CH<sub>3</sub>SH effectively and could fix a large amount of generated SO<sub>4</sub><sup>2-</sup> with its large capacity.

In conclusion, the removal of CH<sub>3</sub>SH using a photocatalyst–excimer–lamp hybrid reactor was investigated. Much higher efficiency and continuous treatment without declining the

efficiency was achieved. Although we used a simple and small reactor with conventional methods and conditions, for example, atmospheric pressure and a mercury-free UV-source, it would be attractive to develop a similar continuous-type air purification system for the practical treatment of highly CH<sub>3</sub>SH contaminated environments, such as a refrigerator. Real odor samples such as kimchi were also prepared and successfully treated with the reactor in a refrigerator.

## Notes and references

- 1 A. Fujishima and K. Honda, *Nature*, 1972, **238**, 37.
- 2 A. Fujishima, T. N. Rao and D. A. Tryk, *J. Photochem. Photobiol., C*, 2000, **1**, 1.
- 3 A. Fujishima, X. Zhang and D. A. Tryk, *Surf. Sci. Rep.*, 2008, **63**, 515.
- 4 T. Ochiai, T. Hoshi, H. Slimen, K. Nakata, T. Murakami, H. Tatejima, Y. Koide, A. Houas, T. Horie, Y. Morito and A. Fujishima, *Catal. Sci. Technol.*, 2011, DOI: 10.1039/C1CY00185J.
- 5 U. Kogelschatz, *Pure Appl. Chem.*, 1990, **62**, 1667.
- 6 N. Spyrou and C. Manassis, *J. Phys. D: Appl. Phys.*, 1989, **22**, 120.
- 7 H.-H. Kim, Y.-H. Lee, A. Ogata and S. Futamura, *Catal. Commun.*, 2003, **4**, 347.
- 8 T.-X. Liu, X.-Z. Li and F.-B. Li, *Ind. Eng. Chem. Res.*, 2010, **49**, 3617.