**ICESP X – Australia 2006**
**Paper 2C3**

# NOx REMOVAL USING DBD WITH UREA SOLUTION AND PLASMA TREATED $TiO_2$ PHOTO CATALYST

**T SAKAMAKI, H MURATA AND S KOGOSHI**
**Tokyo University of Science**
**contact_kogoshi@ee.noda.tus.ac.jp**

## ABSTRACT

Two kinds of experiments for NOx removal have been carried out. One is the experiment using dielectric barrier discharge (DBD) with the aid of adding urea solution. The other is the experiment with plasma treated $TiO_2$ photo catalyst. For adding urea solution the energy efficiency of NOx removal by DBD is better than without the adding by more than 10 times at Vac ~7.2kV. The adding water only also shows good result. So the improvement in NOx removal by DBD with urea solution is not only due to urea but also water. $TiO_2$ films are developed on the one side of a quartz tube at 500$^o$C by use of the sol-gel method. Then the $TiO_2$ films have been processed in hydrogen or nitrogen plasma. The difference of NOx removal rate between the plasma treated films and no treated films has been measured, in which measurements a chemical lamp, black light and fluorescent lamp were used. The results show that the hydrogen plasma treated film is the most efficient as photo catalyst for NOx removal.

## INTRODUCTION

The harmful effects of NOx(NO and $NO_2$) such as the formations of photochemical smog and acid rain as well as unfavourable effects on human respiratory system are well known. NOx is formed in all combustion processes from the high temperature reaction between $N_2$ and $O_2$.

Two kinds of experiments for NOx removal have been carried out. One is the experiment using dielectric barrier discharge (DBD) with the aid of adding urea solution. The other is the experiment with plasma treated $TiO_2$ photo catalyst.

The selective catalytic reduction(SCR) of NOx with a reducing agent, i.e. $NH_3$ is one of the most successful technique for the removal of NOx in power generation plants.

The $NH_3$ selectively reacts with NOx components of an exhaust gas without reacting with $O_2$ (Bosch and Janssen (1988)). However, it would not be possible to use $NH_3$ on a diesel powered car because it is corrosive, toxic and difficult to store, transport and handle. It has been proposed that $NH_3$ could be replaced by aqueous solutions of urea ($(NH_2)_2CO$) by Held, Konning and Puppe (1990) and much interest has been focused on using urea as a safer source of ammonia in automotive applications (for example Sullivan and Doherty (2005),Li, Jones, Grassian and Larsen (2005)) .

On the other hand Takei et al (1998) proposed to reduce NOx without any catalysts but with urea. But it requires high temperature (800~1000.) and high concentration of $NH_3$. We think that NOx could be reduced by dielectric barrier discharge with aqueous solution of urea without any catalysts at room temperature.

$TiO_2$ is also known to remove NOx by oxidizing NO to $NO_2$ and $NO_2$ being adsorbed by active carbon for example. It was found by Masuo and Kato (1959) that substances on $TiO_2$ were photo-oxidized. However, $TiO_2$ can only be activated by UV light (<380nm). It is more useful if $TiO_2$ can be activated by visible light as well as UV light. Nitrogen-doped $TiO_2$ ($TiO_{2-x}N_x$)(Morikawa et al (2005)) and declined composition of the O/Ti $TiO_2$ ($TiO_2$(surface) to $TiO_{1.9}$(bottom)) (Kitano et al (2005)) have been proposed as practical visible light-responsive $TiO_2$. Those $TiO_2$ thin films were prepared on glass substrates, for example, by sputtering a $TiO_2$ target in an $N_2$(40%)/Ar gas (the former) and Ar gas (the latter). In the present work, $TiO_2$ thin films were prepared by use of the sol-gel method and then the films were reformed by exposed to $N_2$ or $H_2$ plasma, which were produced by a surface wave plasma source.

In this paper, first the NOx removal experiments using DBD with urea solution and then visible light sensitive $TiO_2$ film will be reported.

## EXPERIMENTS AND RESULTS

### NOx Removal by DBD with Urea Solution

#### *Experiment*

Fig.1 shows the experimental setup for NOx removal by DBD with urea solutions. The discharge tube made of pyrex glass (inner diameter: 19.5 mm.,outer diameter: 23.0 mm., length: 200 mm.) is wounded by Cu foil, which works as an outer electrode. A screw rod made of brass (2mm.) is set at the centre of the discharge tube as an inner electrode. AC high voltage (50Hz, 7-11 $kV_{p-p}$ ) was applied between the two electrodes and then DBD took place inside the tube. The mimic exhaust gas ($N_2$ (NO:780ppm included):1000cc/min, $O_2$:125cc/min) is run into the discharge tube after through a bubbling pot which contains water or an aqueous urea solution or nothing. The concentrations of NO and NOx after passing through the discharge tube are measured by a NOx detector (testo350., TESTO). The weight of urea dissolved in water is 10 – 50g/100ml.

### *Results*

The dependence of the NO removal rate on the urea concentration in an aqueous solution is shown in Fig.2. The parameters in Fig. 2 are the weight percentage (= (urea weight)/(urea + water weight)*100). One can see that the most effective concentration for NO removal is about 23%. Figure 3 compares NO removal rates among no adding, water adding and an aqueous urea solution (concentration 23%) adding. This graph indicates that adding an aqueous urea solution is effective for NO removal.

## NOx Removal by $TiO_2$ Thin Film

### *Experiment*

A $TiO_2$ thin film was sintered on the one side of a half quartz tube at 500 . by use of the sol-gel method. The detail how to make a $TiO_2$ film on the tube was found elsewhere (Katamoto et al (2004)). Then the $TiO_2$ thin film was processed by $H_2$ or $N_2$ plasma to be responsible to visible light. After that the half of quartz tube was sticked with another half of a clear quartz tube without any $TiO_2$ films. A surface wave plasma source is used for processing the $TiO_2$ film and the setup of the plasma source is shown in Fig.4. The parameters of the plasma source are listed in Table1. The detail of the plasma source (a surface wave plasma source) is described elsewhere (Takahashi (2003)).

*Table 1: Parameters of plasma source*

| | |
|---|---|
| Gas spices | $H_2$ or $N_2$ |
| Gas pressure | 1 torr |
| Microwave power | 100 W |
| Microwave frequency | 2.45 GHz |
| Plasma exposure time | 30 min. |

The NO removal experimental setup with the $TiO_2$ photo catalyst is shown in Fig.5. The reactor made of a quartz tube (inner diameter: 19.5 mm.,outer diameter: 22.5 mm., length: 120 mm.), a half of which is coated by a $TiO_2$ film, is irradiated by three kinds of fluorescent lamps. They are an ordinary fluorescent lamp (FL6D, TOSHIBA Co.), a chemical lamp (FL10BL, TOSHIBA Co.) and a black lamp (FLBLB, TOSHIBA Co.). The mimic exhaust gas ($N_2$ (NO:780ppm included):1000cc/min, $O_2$:125cc/min) is run into the reactor tube through a bubbling pot which contains water. The concentrations of NO and NOx after passing through the reactor tube are measured by a NOx detector (test 350, TESTO).

### *Results*

Table 2 shows the comparison of NO removal rates among an ordinary $TiO_2$ film, a $H_2$ plasma processed film and a $N_2$ plasma processed $TiO_2$ film. For the ordinary fluorescent lamp no processed $TiO_2$ film almost can't oxidize NO. The best value is obtained in the case of $H_2$ plasma processed $TiO_2$ film with the chemical lamp (FL10BL).

*Table 2: Comparison of NO removal rate among different $TiO_2$ films*

| | No processed $TiO_2$ film | $H_2$ plasma processed one | $N_2$ plasma processed one |
|---|---|---|---|
| Fluo. lamp | 0.08 % | 1.05 % | 0.93 % |
| Chemical lamp | 0.76 % | 1.32 % | 1.24 % |
| Black lamp | 0.59 % | 0.99 % | 0.98 % |

## SUMMARY

In NOx removal by DBD it is effective to add urea solution and in the present experiment the most effective concentration of urea in an aqueous solution is 23%.

$H_2$ or $N_2$ plasma treated $TiO_2$ thin films can be activated by an ordinary fluorescent lamp and oxidize NO.

## ACKNOWLEDGMENTS

The authors thank Ms. Yokoyama K., Mrs. Kozuka S. and Hirohashi S. for providing $TiO_2$ thin films.

## REFERENCES

Bosch H. And Janssen F. (1988). Catal. Today, **2**, 369, 1988.
Held W., Konning T. And Puppe L. (1990). SAE Paper, **900**, 496, 1990.
Sullivan J. A. And Doherty J. A. (2005). Applied Catalysis B: Environmental, **55**, 185-194,2005.
Li G., Jones C. A., Grassian V. H. And Larsen S. C. (2005). Journal of Catalysis, **234**, 401-413,2005.
Takei M. et al (1998). Proc. of 30th Chemical Engineering autumn meeting, 262, 1998.
Masuo F. and Kato S. (1959). US Patent, No.2910415, 1959.
Morikawa K., Asahi R, Ohwaki T., Aoki K. Suzuki K. and Taga Y. (2005). R&D Review of Toyota CRDL, **40**, 45-50,2005.
Katamoto T., Kogoshi S. and Haruyama O. (2004). J. Institute of Electrostatics Japan, **28**, 30-34, 2004.
Takahashi Y. and Kogoshi S. (2004). IEEJ Transaction on Fundamental and Materials, **123-A**, 1240-1245, 2003.

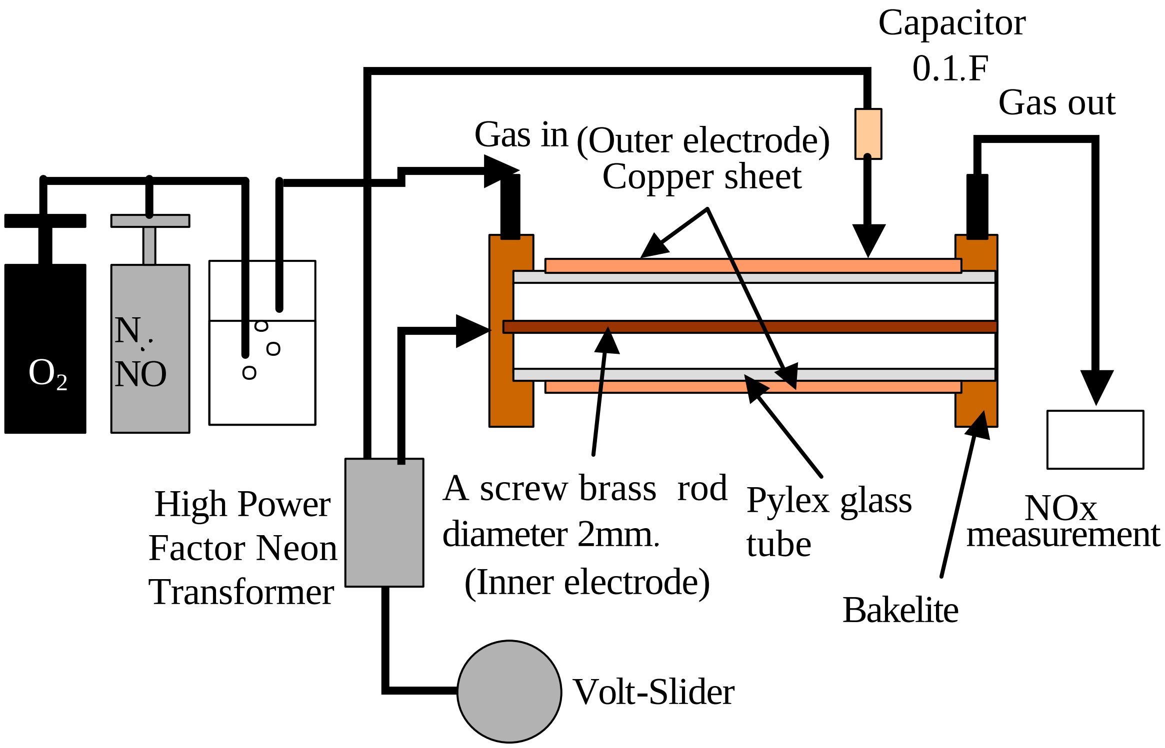

*Figure 1: DBD experimental setup*

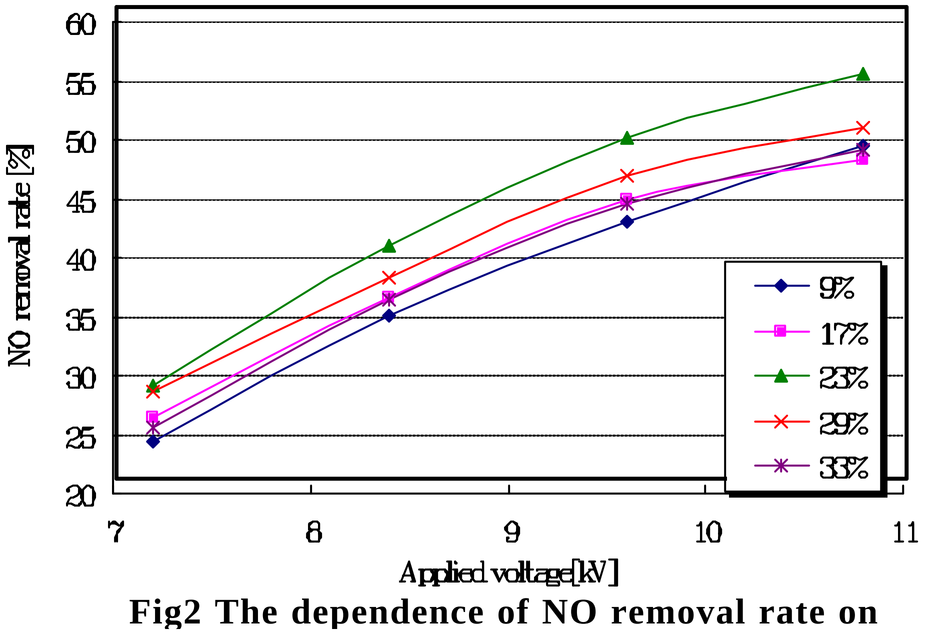

*Figure 2: Dependence of NO removal rate on urea concentration*

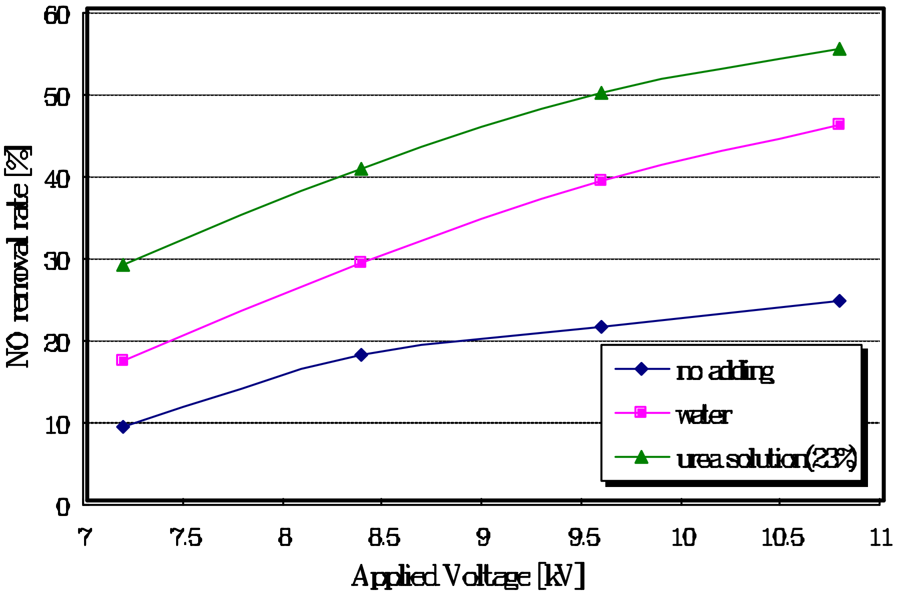

**Fig3 The dependence of NO removal rate**

*Figure 3: Dependence of NO removal rate on applied voltage*

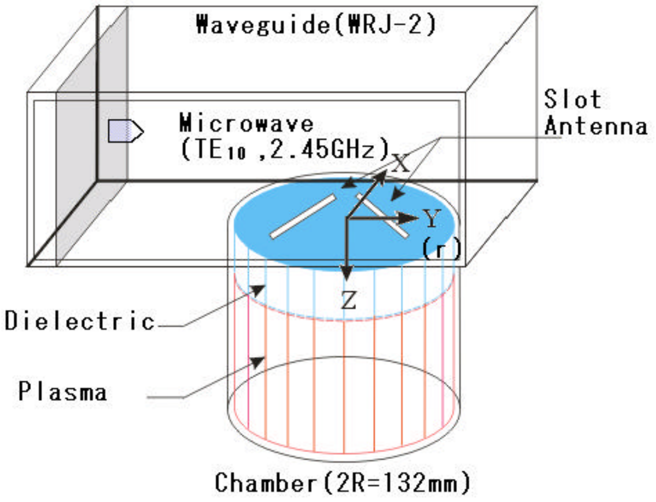

*Figure 4: Surface wave plasma source setup*

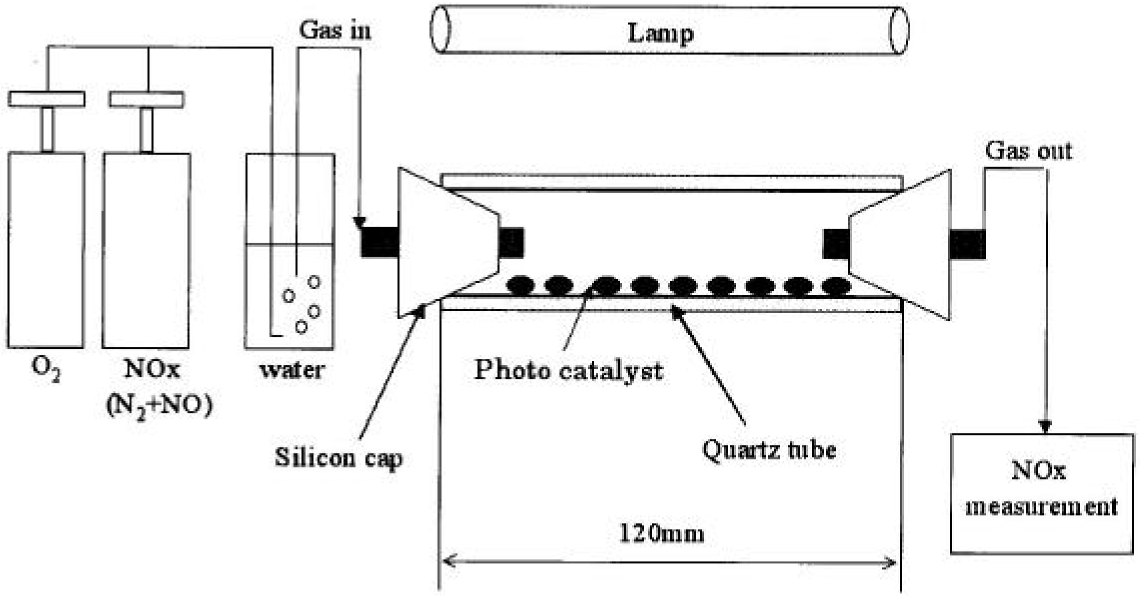

*Figure 5: NO removal experimental setup with $TiO_2$ film*