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NO and SO_2 removal in non-thermal plasma reactor packed with glass beads-TiO_2 thin film coated by PCVD process

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ABSTRACT

We analyzed the NO and SO_2 removal in the non-thermal plasma discharge process combined with TiO_2 photocatalyst. The non-thermal plasmas were generated by dielectric barrier discharge with glass beads as dielectric materials. The TiO_2 thin films were coated on the glass beads uniformly without crack by a rotating cylindrical plasma chemical vapor deposition reactor. The NO and SO_2 removal efficiencies obtained in non-thermal plasma–TiO_2 photocatalysts hybrid system were higher than those in plasma process only, because of the additional removal of NO and SO_2 by photocatalysts. The NO and SO_2 removal efficiencies become higher, as applied peak voltage, pulse frequency and gas residence time increase, or as the initial NO and SO_2 concentrations decrease. The hybrid system of non-thermal plasma and photocatalyst thin film on glass beads prepared by PCVD process is quite efficient method to remove NO and SO_2.

1. Introduction

Increasing concern over the emission of air pollutants into the atmosphere has motivated the research into environmentally acceptable and energy-efficient methods to remove these gases from atmospheric pressure gas streams. Non-thermal plasma technique has the great possibility to realize the pollution control of exhaust gases [1–4]. Non-thermal plasmas can be produced by electrical discharge in which a majority of the electrical energy goes into the production of energetic electrons, rather than into gas heating. In the non-thermal plasmas even though the electrons are short-lived under atmospheric pressure conditions and rarely collide with the pollutant molecules, they undergo many collisions with the dominant background gas molecules (N_2, O_2, H_2O) and produce reactive radicals ($N^\bullet$, $O^\bullet$, $OH^\bullet$, $O_3{}^\bullet$, $HO_2{}^\bullet$ etc.) by electron-impact dissociation and ionization reactions. The NO and SO_2 decompose by the reactions with these reactive radicals ($NO + O + M \rightarrow NO_2 + M$, $NO + O_3 \rightarrow NO_2 + O_2$, $O + SO_2 + M \rightarrow SO_3 + M$ and $SO_2 + O_3 \rightarrow SO_3 + O_2$) to produce mainly NO_2 and SO_3 as products [5,6].

There are several researches to improve the removal efficiencies of air pollutants by the combination of non-thermal plasmas and catalysis process [7–12]. Ogata et al. [8] investigated the effective combination of plasma energy and solid surface properties, such as catalysis and adsorption, in the packed-bed type catalyst and adsorbent-hybrid reactors with a mixture of $BaTiO_3$ pellets and other ceramic pellets as a catalyst or adsorbent. They showed that using catalysts and adsorbents in the plasma reactor enhanced the product selectivity and the energy efficiency. Mok et al. [9] studied the removal of nitrogen oxides (NO_x) using a non-thermal plasma reactor (dielectric-packed bed reactor) combined with monolith V_2O_5/TiO_2 catalyst and found that the combination of non-thermal plasmas with selective catalytic reduction enhanced the NO_x removal efficiency at low temperatures. Dors and Mizeraczyk [10] analyzed NO_x removal process in a dc corona discharge-V_2O_5 and TiO_2 catalyst hybrid system at a room temperature in the presence of ammonia and showed the remarkable NO_x removal efficiencies in the dc corona discharge–catalyst hybrid system, compared with those in the dc corona discharge reactor only.

The removal of air pollutants, such as NO and SO_2, can also be enhanced by the combination of non-thermal plasma process and TiO_2 photocalalysts. TiO_2 nanoparticles are well known photocatalysts which exhibit a band gap (3.2 eV) and cover the redox potential of the H_2O/OH couple (−2.8 eV), thus promoting the breakdown of many compounds. The TiO_2, particularly in the anatase form, acts as the photocatalyst under ultraviolet light exposure. Irradiation with photons, which have energy greater than the TiO_2 bandgap energy, can generate the charge carrier pairs, holes and electrons. Both electrons and holes are very powerful reductants and oxidants to react with the hazardous gases [13]. Non-thermal plasma can be a source of UV light for activation of TiO_2 photocatalysts in non-thermal plasma–photocatalysts hybrid system. Kim's group analyzed the NO and SO_2 removal in dielectric bar-

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rier discharge–TiO_2 photocatalysts hybrid system and they coated TiO_2 photocatalysts (Degussa P-25) on dielectric glass beads by dip-coating method and showed that NO and SO_2 removal efficiencies in dielectric barrier discharge–photocatalysts hybrid system were higher than in plasma process only [11,12].

For high efficiency of air pollutant removal in the non-thermal plasma–TiO_2 photocatalysts hybrid system, it is quite important to coat the TiO_2 photocatalysts uniformly on the surface of glass beads by using an efficient particle coating process. There are several kinds of coating processes on various types of substrates, such as anodization [14], electrodeposition [15], sol–gel [16], dip-coating [12], activated reactive evaporation [17], reactive dc magnetron sputtering [18], chemical vapor deposition (CVD) [19–22], flame-coating [23], fluidization [24], electrostatic sol-spray deposition [25] and spray pyrolysis [26]. Among the abovementioned coating processes, sol–gel, dip-coating, flame-coating, fluidization and plasma CVD (PCVD) methods can be applied for particle coating. The PCVD technique, as a dry particle coating process, has several advantages, such as uniformity, high throughput, relatively low cost, and good control of the deposition parameters. In the rotating cylindrical PCVD reactor, the particles will rotate together with the reactor and some particles may stay in the gas phase of the bulk plasma. For the particles falling down in the bulk plasma of the gas phase, their total surface area is available for deposition and the particles are coated uniformly with the precursors generated by the plasma reactions. Kim et al. [27–29] proposed a rotating cylindrical PCVD reactor for uniform particle coating and analyzed the reactor performances numerically.

In this study, we coated the TiO_2 thin films on the glass beads by the rotating cylindrical PCVD reactor and analyzed the NO and SO_2 removal in non-thermal plasma reactor packed with the TiO_2-coated glass beads. We compared the removal efficiencies of NO and SO_2 in the non-thermal plasma reactor with TiO_2 photocatalysts prepared by the dip-coating and PCVD methods and also without TiO_2 photocatalysts.

2. Experiments

Fig. 1 shows the experimental setup for NO and SO_2 removal by non-thermal plasma reactor packed with TiO_2-coated glass beads. The non-thermal plasma discharge is produced in cylinder-wire type pellet packed-bed reactor. The copper rod wire (5 mm diameter) is located at the center of this glass tube which has the inner and outer diameters of 27 and 30 mm, respectively. The outside wall of the reactor is wrapped over by a stainless steel mesh which acts as a ground electrode. The non-thermal plasmas were generated by applying high voltage power into the reactor. All gas flow rates were controlled by mass flow controllers (MFC) (Model FC-280S, USA, Tylan). Each gas stream passed through the moisture trap (silica gel). The concentrations of NO and SO_2 in the outlet were measured by an electro-chemical gas analyzer (Eurotron, GreenLine MK II). The high voltage applied to the discharge electrode was measured by a 1000:1 high-voltage probe (PVM-4, North Star Research) and a digital oscilloscope (TDS 220, Tektronix).

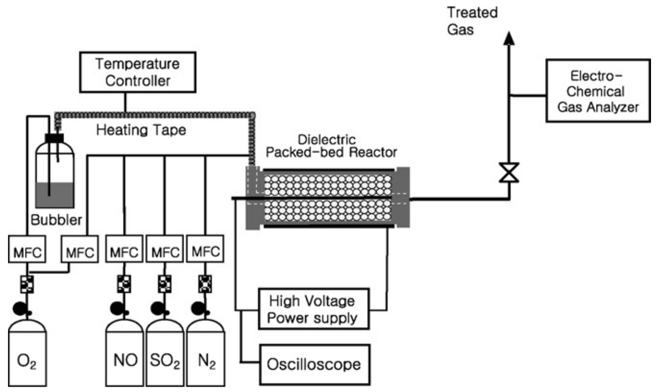

Fig. 1. Experimental setup for NO and SO_2 removal by using non-thermal plasma–TiO_2 photocatalysts hybrid system.

The glass beads (3 mm diameter) as dielectric materials were coated by TiO_2 photocatalyst thin film by the rotating cylindrical PCVD reactor. The PCVD reactor is the quartz cylinder with inner diameter and the length of 55 and 280 mm, respectively. The inductively coupled plasmas are generated by applying the electric rf power to a water-cooled spiral-shape coil electrode which is located outside the cylindrical reactor. The precursor for the TiO_2 thin films is titanium tetraisopropoxide (TTIP). The flow rate of TTIP as a source of Ti was controlled by changing the power of ultrasonic nebulizer, and the N_2 gas was used as the carrier gas for TTIP. O_2 was supplied to the reactor separately from TTIP to prevent reaction between O_2 and TTIP in the feed line. The flow rates of all gases were controlled by MFCs. Glass beads coated with TiO_2 thin films in PCVD reactor were then annealed at 500 °C for 1 h [29,30].

3. Results and discussion

To coat the TiO_2 thin films on the glass bead by the PCVD reactor, the following experimental conditions were applied: deposition time, mass flow rate of TTIP, applied electric power, reactor pressure and rotation speed of reactor were 60 min, 2.667 mg/min, 10 W, 600 mtorr and 10 rpm, respectively. Fig. 2 shows SEM images of the

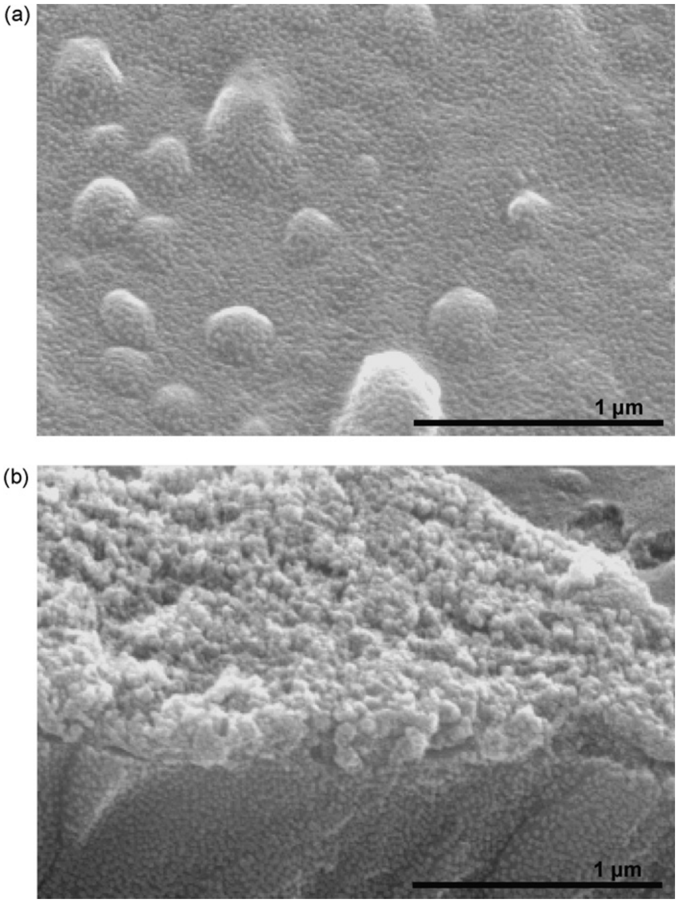

Fig. 2. SEM images of (a) surface and (b) cross-section of glass beads coated with TiO_2 thin film by a rotating cylindrical PCVD reactor after heat treatment.

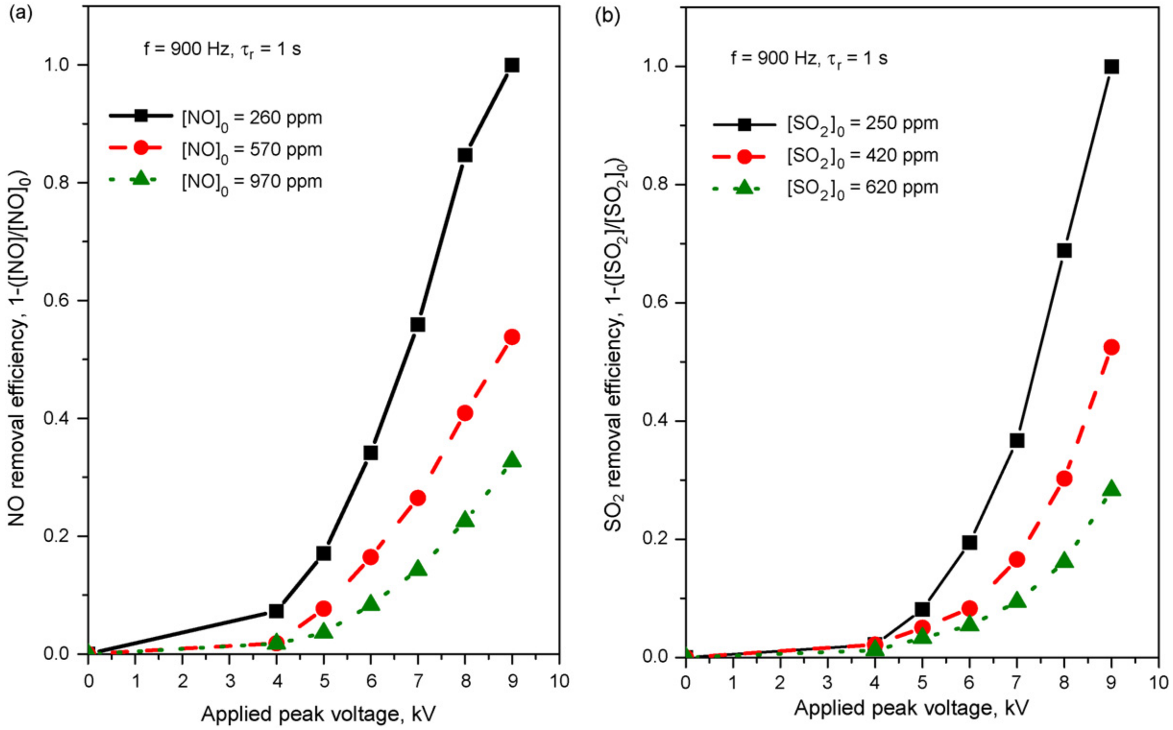

Fig. 3. (a) NO and (b) SO_2 removal efficiencies for various NO and SO_2 initial concentrations as a function of applied peak voltage.

surface and cross-section of TiO_2 thin films after heat treatment. The TiO_2 thin films were coated on the glass beads well without crack and the thickness of TiO_2 thin film was about 150 nm.

For NO and SO_2 removal experiments, the standard conditions of initial NO concentration ($[NO]_0$), initial SO_2 concentration ($[SO_2]_0$), pulse frequency (f) and residence time of gas stream (τ_r) were 570 ppm, 420 ppm, 900 Hz, and 1 s, respectively. The O_2 concentration was controlled to become 21% and the N_2 was the balance gas. The total gas flow rate and the gas temperature were 5 l/min and 298 K, respectively. The applied peak voltage varied from 3 to 13 kV. All experiments were done at 1 atm.

Fig. 3 shows the effects of applied peak voltage on NO and SO_2 removal for various initial NO and SO_2 concentrations. As the applied voltage increases, the electron-impact dissociation reaction

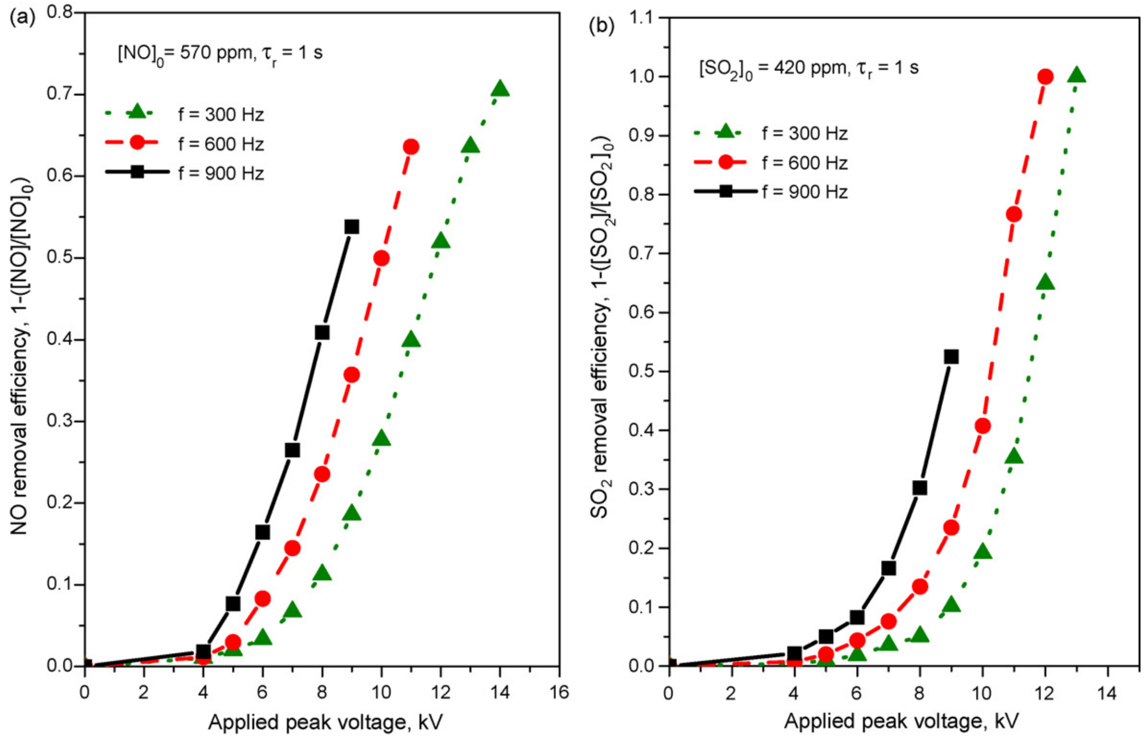

Fig. 4. (a) NO and (b) SO_2 removal efficiencies for various pulse frequencies as a function of applied peak voltage.

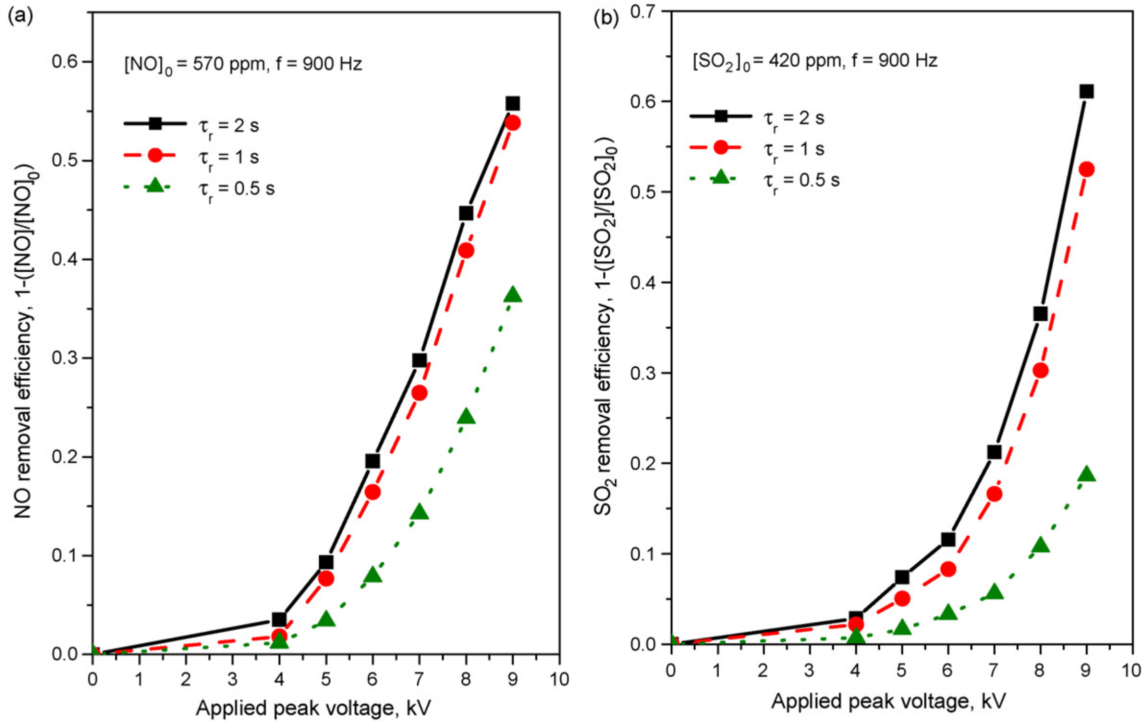

Fig. 5. (a) NO and (b) SO_2 removal efficiencies for various residence times as a function of applied peak voltage.

rates for radical (O, N, OH, H etc.) generation increase, because the electron energy for those radical generation becomes higher, and, as a result, the concentrations of reactive radicals increase and the NO and SO_2 removal efficiencies increase by the faster oxidation reactions of NO and SO_2 with those reactive radicals. At $[NO]_0 = 260$ ppm or $[SO_2]_0 = 250$ ppm, the removal efficiencies of NO and SO_2 at the peak voltage of 9 kV almost reaches 100%, because the energy supplied to dielectric barrier discharge reactor is enough to decompose all NO and SO_2 molecules. With the increases of initial NO and SO_2 concentrations, the number of molecules to be removed increases, while the amount of supplied energy is kept constant, and, consequently, the number of energetic electrons produced in plasma region is the same for each condition. As the total amount of NO and SO_2 increases, the number of molecules not decomposed increases, which makes the removal efficiencies of NO and SO_2 decrease with the increases of initial NO and SO_2 concentrations.

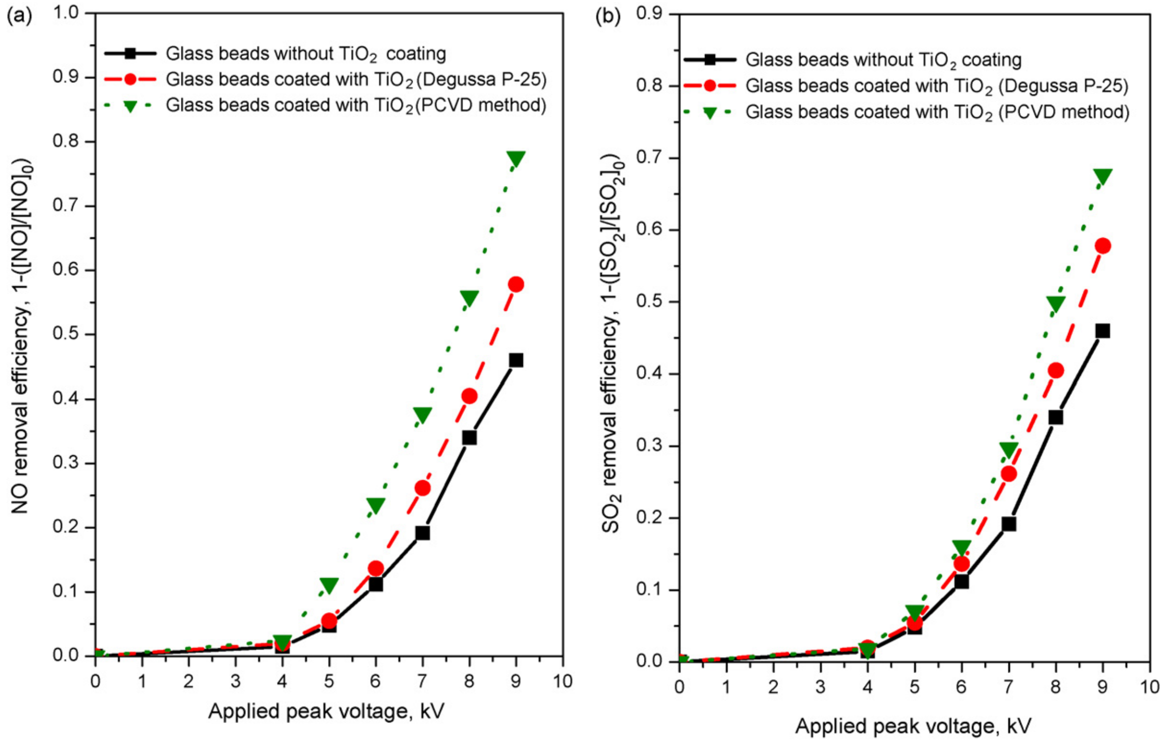

Fig. 6. (a) NO and (b) SO_2 removal efficiencies as a function of applied peak voltage with TiO_2 photocatalysts by 2 different coating methods and without TiO_2 photocatalysts.

Fig. 4 shows the NO and SO_2 removal efficiencies as a function of applied peak voltage for various pulse frequencies. Three pulse frequencies (300, 600 and 900 Hz) were applied in these experiments and the pulse frequency of 900 Hz was most effective for NO and SO_2 decomposition. The increase in pulse frequency enhances the NO and SO_2 removal efficiencies, because more number of microdischarges is generated between the packed dielectric materials resulting in the faster production of reactive radicals at the higher frequencies.

Fig. 5 shows the NO and SO_2 removal efficiencies as a function of applied voltage for the gas flow rates of 2.5, 5 and 10 l/min, which are equivalent to the gas residence times of 2, 1 and 0.5 s inside the reactor, respectively. As the gas residence time increases, the plasma reactions for NO and SO_2 removal take place for a longer time in the reactor and the NO and SO_2 removal efficiencies increase.

Fig. 6 shows the comparison of NO and SO_2 removal efficiencies with TiO_2 photocatalysts by 2 different coating methods and also without TiO_2 photocatalysts. One method of coating was to dip-coat the glass beads with the commercial TiO_2 photocatalysts (Degussa P-25) [12]. The lowest efficiencies of NO and SO_2 removal were obtained for the plasma process only without using any photocatalysts, because the UV light generated inside the plasma process could not be used to remove the NO and SO_2 additionally. For the non-thermal plasma–TiO_2 photocatalysts hybrid system, the NO and SO_2 removal efficiencies with the glass beads coated by the PCVD method become higher than those by the dip-coating method, because the more uniformity and larger surface area of TiO_2 thin film was obtained by PCVD method. Fig. 6 shows that the rotating PCVD reactor process can be an effective method to make uniform coating onto glass beads and also that the non-thermal plasma process with the TiO_2 coated glass beads can be a powerful method to remove NO and SO_2 efficiently.

4. Conclusions

We analyzed the effects of several process variables on NO and SO_2 removal in the non-thermal plasma–TiO_2 photocatalysts hybrid system. The TiO_2 thin film was coated on the glass beads uniformly without cracks by a rotating cylindrical PCVD reactor. As the initial NO and SO_2 concentrations increase or as the gas residence time decreases, the removal efficiencies of NO and SO_2 both decrease. The NO and SO_2 removal efficiencies increase with the increase of the applied pulse frequency. In this study, the removal efficiencies of NO and SO_2 were almost 100% for the following experimental conditions: $[NO]_0 = 260$ ppm, $[SO_2]_0 = 250$ ppm, $f = 900$ Hz, and $\tau_r = 1$ s. We can propose that the non-thermal plasma reactor packed with the dielectric glass beads-TiO_2 thin film coated by PCVD process can be an effective method to remove NO and SO_2.

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