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Electrical and spectroscopic diagnostics of a single-stage plasma-catalysis system: effect of packing with TiO₂

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Abstract
The influence of adding TiO₂ on the electrical and spectroscopic characteristics of a N₂ dielectric barrier discharge (DBD) has been investigated in a single-stage plasma-catalysis system. The introduction of the catalyst into the electrode gap leads to a transition in the discharge behaviour. The presence of the TiO₂ pellets in the discharge significantly increases the vibrational temperature of N₂ in the DBD, which suggests that the interaction of plasma and catalyst has a strong effect on the electron energy distribution function in the discharge with an increase in electron density in the high-energy tail of the distribution function.

(Some figures may appear in colour only in the online journal)

In the past decade, the application of plasma catalysis for the destruction of gas pollutants and hydrocarbon conversion has attracted considerable interest [1–5]. The interactions between plasma and catalyst become very complex when the catalyst is placed directly in the plasma. The integration of plasma and catalysis can sometimes generate a synergistic effect, which has been successfully proven to enhance the destruction of the pollutants and improve the selectivities towards the desired end-products [6–8]. Plasma-catalysis can also activate catalysts at low temperature thereby increasing the energy efficiency of the process. Recently, this idea has been extended to the preparation and treatment of catalysts to improve the activity and stability of the catalyst [9, 10]. However, the detailed understanding of the fundamental mechanism of plasma catalysis from both a chemical and physical perspective is still very patchy [3]. Until now, studies have mainly focused on the plasma-catalytic chemical reactions to maximize the process performance, whilst less attention has been paid to the interactions between plasma and catalyst, especially the influence of the catalyst on the fundamental physical characteristics of the plasma [5, 11–13]. The changes in the discharge behaviour due to the presence of a catalyst will in

turn affect the interactions between plasma and catalyst and hence the plasma-catalytic process.

In this study, we have developed a cylindrical double dielectric barrier discharge (DBD) reactor, in which pellets of the TiO₂ are directly packed into the entire discharge gap, known as a single-stage plasma-catalysis configuration. This kind of plasma system has been widely used for plasma-photocatalytic chemical reactions such as the destruction of pollutants in waste gas streams [3]. The influence of the TiO₂ on the physical characteristics of the nitrogen DBD has been investigated by a combination of electrical and optical emission spectroscopic diagnostics.

Figure 1 shows a schematic diagram of the experimental setup. The experiment is carried out in a cylindrical DBD reactor, as described in detail in our previous work [5]. The DBD reactor consists of two coaxial quartz tubes, both of which are covered by a stainless steel mesh electrode over a length of 50 mm. The inner electrode is connected to a high voltage output and the outer electrode is grounded via an external capacitor C_{ext} (42.4 nF). The discharge gap is fixed at 1.5 mm with a total discharge volume (V_t) of 5.5 cm³. The nitrogen flow rate is varied between 0.1 and 1 L min⁻¹. The

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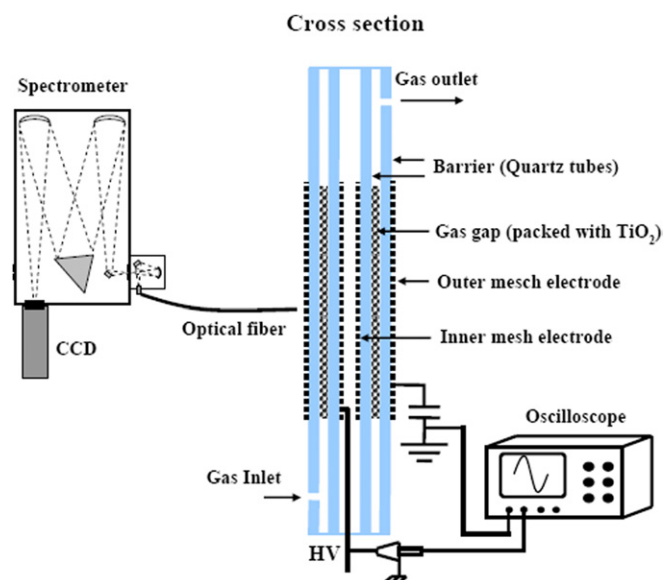
Figure 1. Schematic diagram of the experimental setup.

DBD reactor is supplied by a maximum peak-to-peak voltage of 24 kV at a variable frequency of 30–40 kHz. Anatase TiO_2 pellets (Alfa Aesar) with diameter between 500 and 850 μm are packed into the entire discharge gap. The Brunauer–Emmett–Teller (BET) surface area of the TiO_2 is 137 $m^2 g^{-1}$ [2]. In this typical single-stage plasma-catalysis system, the DBD gap consists of two parts: a small gaseous volume (V_g) and large volume of the solid catalyst (V_c) with a low void fraction ($\varepsilon = V_g/V_t$). The applied voltage (U_a) is measured by a high voltage probe, while the total current (I_t) is recorded by a Rogowski-type current monitor (Pearson Model 110). The voltage (U_c) on the external capacitor is measured to obtain the charge generated in the discharge. All the electrical signals are sampled by a four-channel digital oscilloscope (Tektronics TDS 2014). A LABVIEW control system is used for the online real-time measurement of discharge power by the area calculation of Q-U Lissajous figure. An equivalent electrical circuit of the DBD reactor can be found in [5]. Emission spectra of the discharge are recorded by an optical fibre connected to a Jarrell-Ash MonoSpec 27 spectrometer with a wide spectral range from 250 to 900 nm.

Figure 2 shows the electrical signals of the N_2 DBD with and without TiO_2 catalyst at a fixed discharge power of 70 W. It is interesting to note that the presence of the TiO_2 in the discharge significantly decreases the number and amplitude of the current pulses, which suggests that fully packing the catalyst pellets into the gap suppresses the formation of filamentary microdischarges due to the significantly reduced discharge volume in the gap. As a result, filaments can only be generated non-uniformly in the void space between the catalyst pellets and the pellet-quartz barrier. In addition, surface discharges are generated simultaneously over the surface of the catalyst pellets due to the packed-bed effect. The emission intensity of the surface discharges is much weaker than that of the filamentary discharges generated between the pellets and the pellet-quartz wall. An increase in the applied voltage or discharge power is found to enlarge the discharge area on the
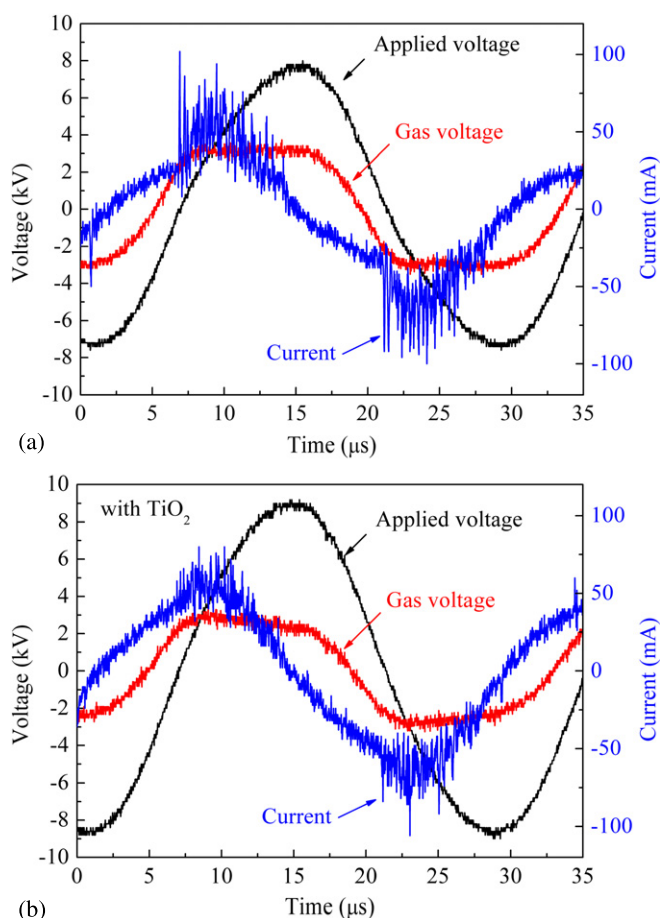
Figure 2. Electrical signals (current and voltage) of the nitrogen DBD: (a) without packing; (b) with TiO_2 catalyst (discharge power 70 W).

catalyst surface. These phenomena indicate that introducing TiO_2 pellets into the discharge gap leads to a transition of the discharge behaviour due to a significant change in the void fraction in the gap. The discharge with fully packed TiO_2 catalyst is a combination of a surface discharge on the surface of the catalyst pellets and spatially limited microdischarges generated in the void space between the pellets and the pellet-quartz barrier. Similar change in the discharge behaviour has also been observed when both non-conductive (Al_2O_3, zeolite 3A and NiO/Al_2O_3) and conductive (reduced $Ni//Al_2O_3$) materials are fully packed into the similar single-stage plasma-catalysis reactor [5, 14]. In contrast, the current profile of the discharge filled with porous quartz wool or packed with small pieces of catalyst in flake form still exhibits a similar discharge mode with as strong a microdischarge as the DBD without packing [14, 15]. The relative contribution of filamentary and surface discharges is likely to depend on many factors including particle size, particle shape and packing location, and hence the void fraction of the electrode gap.

Figure 3 shows that despite the constant dissipated power (70 W) in the plasma, the applied voltage increases from 15.4 $kV_{pk–pk}$, in the case of no packing to 17.8 $kV_{pk–pk}$ with the TiO_2 catalyst. This change suggests that fully packing TiO_2 into the gas gap requires higher input power and applied voltage to sustain the discharge at the same discharge power.

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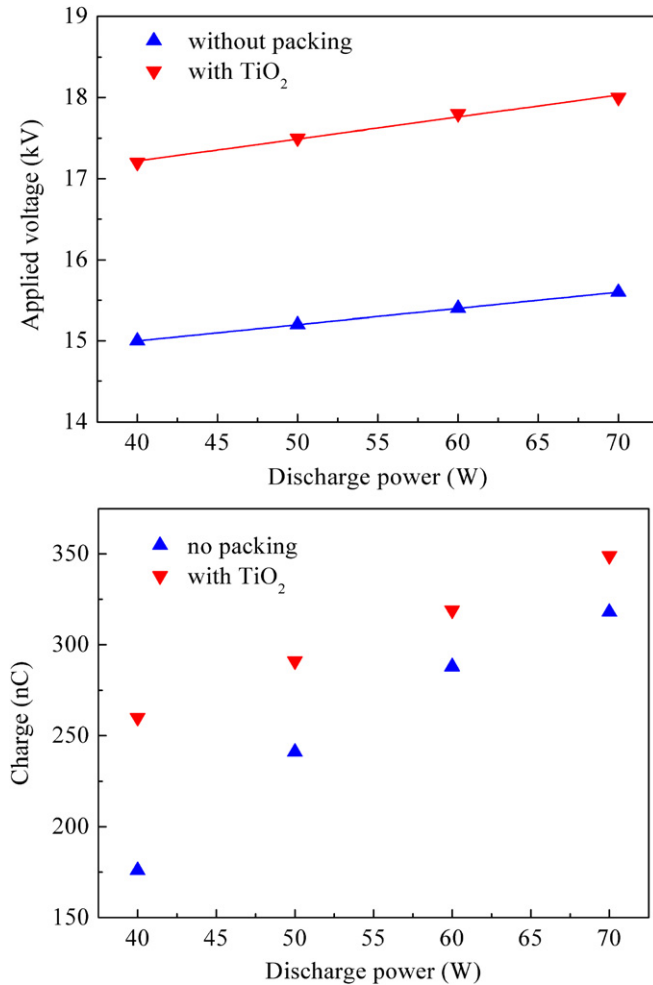
Figure 3. Effect of packing TiO_2 catalyst on the (*a*) peak-to-peak applied voltage and (*b*) charge generated per half cycle of the applied voltage.

This phenomenon has also been confirmed by packing metal oxide materials such as Al_2O_3 and zeolite 3A into the discharge gap [14]. Given that the discharge power is the same in each case, the current must be smaller in the catalyst packed plasma discharges, which can be confirmed from the electrical signals of the discharge (figure 2).

Figure 3(*b*) shows the influence of TiO_2 catalyst on the charge generation in the N_2 DBD at different power levels. We can see that the charges generated per half cycle of the applied voltage significantly increase with the increase in the discharge power. It is worth noting that packing the TiO_2 catalyst into the discharge gap significantly enhances the peak-to-peak charge and the charge generated per half cycle in the DBD. In a discharge without packing, microdischarge channels bridge the gas gap. The charges are transferred through these channels. However, in the single-stage plasma-catalysis reactor fully packed with TiO_2, there is no defined discharge gap. More charges are inhomogeneously distributed on the catalyst surface in the discharge gap rather than being transferred, which has been demonstrated for packing conductive Ni/Al_2O_3 catalyst [5]. This can also be confirmed by a larger capacitance value (C_g) of 33.3 pF in the gap,

about two times the magnitude of the gap capacitance with no packing (18.7 pF).

Optical emission spectroscopic technique is performed to measure the spectra of the nitrogen DBD without and with TiO_2. Both spectra are clearly dominated by intensive molecular band $N_2(C\,^3\Pi_u \to B\,^3\Pi_g)$ second positive system (SPS, $\Delta v = -4, -3, -2, -1, 0, 1$) within the range of 300–450 nm. The intensity of the N_2^+ ($B\,^2\Sigma_u^+ \to X\,^2\Sigma_g^+$) first negative system (FNS) at 391.4 nm is very weak. Compared with the N_2 DBD without packing, the intensity of the N_2 bands in the discharge is much weaker in the presence of the catalyst TiO_2. This suggests that these wavelengths in the UV range may be absorbed by the TiO_2 acting as a photocatalyst. In addition, weak filamentary discharge resulting from the transition of discharge mode in the presence of the catalyst may also lead to the decrease of the intensity of N_2 molecular bands.

The rotational temperature T_r of the N_2 is determined by a comparison between the experimentally measured molecular band of N_2 ($C\,^3\Pi_u \to B\,^3\Pi_g$, $\Delta v = -1$, at 357 nm) and simulated one by using Specair [16], while the vibrational temperature T_v is obtained from a Boltzmann plot of $\ln(I\lambda/A)$ versus vibrational energy (E) from a group of N_2 SPS vibrational transitions ($\Delta v = -2, -1, 0$). Here I and λ are the line emission intensity and wavelength, respectively. A is the corresponding Frank–Condon factor for the vibrational transitions, which can be found in [17]. The slope of the Boltzmann plot is proportional to $1/T_v$. The difference between the vibrational and rotational temperatures indicates a significant level of non-equilibrium state in the N_2 DBD (figure 4).

In figure 4, we can see the rotational temperature of the N_2 DBD without packing increases with rising discharge power from 40 to 70 W. In contrast, the rotational temperature of the N_2 DBD is almost independent of the discharge power when the TiO_2 pellets are fully packed into the discharge gap. In this case, the discharge power may also be heating the catalyst pellets in the gap and the effect of the discharge power on the rotational temperature of the N_2 in the DBD is minimized. We also find that the vibrational temperature decreases with increasing discharge power due to increased vibrational-translational relaxation at higher discharge power. It is worth noting that packing TiO_2 catalyst pellets into the discharge gap leads to a significant rise in the vibrational temperature of N_2 in the discharge. At 40 W, T_v increases from 2800 K in the case of no packing to 4100 K with the TiO_2 catalyst. This behaviour suggests that the presence of the TiO_2 catalyst in the plasma has a strong effect on the electron energy distribution function in the N_2 DBD. As the vibrational temperature increases, there are more high energetic electrons in the tail of the distribution function. Previous work showed that the average electron energy of the discharge increased with the vibrational temperature [18]. It is expected that packing TiO_2 catalyst in the discharge enhances the average electron energy of the plasma.

In this paper, we have shown the effect of packing photocatalyst TiO_2 on the physical characteristics of the N_2 DBD in a single-stage plasma-catalysis system. Introducing

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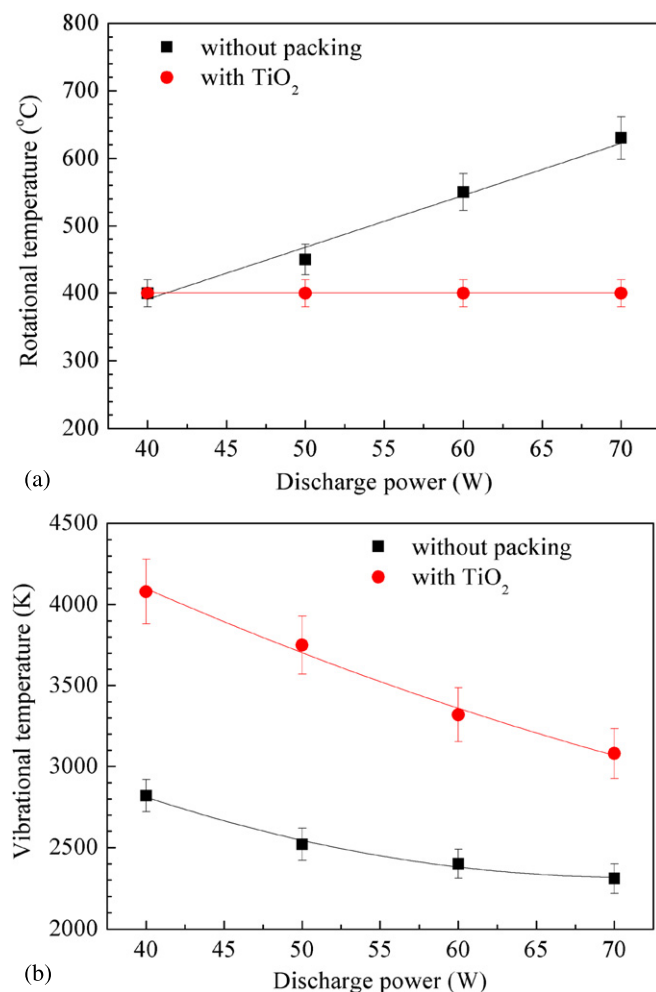
Figure 4. Effect of packing TiO_2 catalyst on the (*a*) rotational and (*b*) vibration temperatures of the nitrogen DBD.

the catalyst pellets into the discharge region leads to a transition of the discharge behaviour from a typical filamentary discharge, to a combination of surface discharge on the surface of the catalyst pellets and spatial limited microdischarges generated in the void space between the pellets and the pellet-quartz. In addition, the results show that the presence of the TiO_2 pellets in the N_2 discharge greatly increases the vibrational temperature of N_2, which suggests the single-stage plasma-catalysis system significantly shift the electron energy

distribution towards rich electrons in the high-energy tail of the distribution function in the N_2 DBD.

References

[1] Harling A M, Glover D J, Whitehead J C and Zhang K 2008 *Environ. Sci. Technol.* **42** 4546
[2] Wallis A E, Whitehead J C and Zhang K 2007 *Appl. Catal. B: Environ.* **74** 111
[3] Whitehead J C 2010 *Pure Appl. Chem.* **82** 1329
[4] Zhang K, Eliasson B and Kogelschatz U 2002 *Indust. Eng. Chem. Res.* **41** 1462
[5] Tu X, Gallon H J, Twigg M V, Gorry P A and Whitehead J C 2011 *J. Phys. D: Appl. Phys.* **44** 274007
[6] Chen H L, Lee H M, Chen S H, Chang M B, Yu S J and Li S N 2009 *Environ. Sci. Technol.* **43** 2216
[7] Chen H L, Lee H M, Chen S H, Chao Y, Chang M B 2008 *Appl. Catal. B: Environ.* **85** 1
[8] Durme J V, Dewulf J, Leys C and Van Langenhove H 2008 *Appl. Catal. B: Environ.* **78** 324
[9] Gallon H J, Tu X, Twigg M V and Whitehead J C 2011 *Appl. Catal. B: Environ.* **106** 616
[10] Zou J J, Zhang Y P and Liu C J 2006 *Langmuir* **22** 11388
[11] Guaitella O, Thevenet F, Guillard C and Rousseau A 2006 *J. Phys. D: Appl. Phys.* **39** 2964
[12] Tu X, Verheyde B, Corthals S, Paulussen S, Sels B F 2011 *Phys. Plasmas* **18** 080702
[13] Kim H H, Kim J H and Ogata A 2009 *J. Phys. D: Appl. Phys.* **42** 135210
[14] Gallon H J, Tu X and Whitehead J C 2011 *Plasma Process. Polym.* DOI: 10.1002/ppap.201100130
[15] Tu X, Gallon H J and Whitehead J C 2011 *20th Int. Symp. Plasma Chemistry (Philadelphia, PA)*
[16] Laux C O, Spence T G, Kruger C H and Zare R N 2003 *Plasma Source Sci. Technol.* **12** 125
[17] Zare R N, Larsson E O and Berg R A 1965 *J. Mol. Spectrosc.* **15** 117
[18] Chen H C, Ali A W and Phelps A V 1985 *Technical Report* (White Oak, MD: Naval Surface Weapons Center)