Plasma-assisted conversion of CO$_2$ in a dielectric barrier discharge reactor: understanding the effect of packing materials

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Abstract

A cylindrical dielectric barrier discharge (DBD) reactor has been developed for the conversion of undiluted CO$_2$ into CO and O$_2$ at atmospheric pressure and low temperatures. Both the physical and chemical effects on reaction performance have been investigated for the addition of BaTiO$_3$ and glass beads into the discharge gap. The presence of these packing materials in the DBD reactor changes the physical characteristics of the discharge and leads to a shift of the discharge mode from a typical filamentary discharge with no packing to a combination of filamentary discharge and surface discharge with packing. Highest CO$_2$ conversion and energy efficiency are achieved when the BaTiO$_3$ beads are fully packed into the discharge gap. It is found that adding the BaTiO$_3$ beads into the plasma system enhances the average electric field and mean electron energy of the CO$_2$ discharge by a factor of 2, which significantly contributes to the enhancement of CO$_2$ conversion, CO yield and energy efficiency of the plasma process. In addition, highly energetic electrons (> 3.0 eV) generated by the discharge could activate BaTiO$_3$ photocatalyst to form electron-hole pairs on its surface, which contributes to the enhanced conversion of CO$_2$.

Keywords
CO$_2$ conversion; Dielectric barrier discharge; Packed-bed effect; Packing materials
1. Introduction

Carbon dioxide (CO$_2$) has been recognised as one of the major contributors to the greenhouse gas effect and its concentration in atmosphere is continuously increasing due to the use of fossil fuels. The UK emits more than 470 million tonnes of CO$_2$ per year and of this 39% is emitted by the energy and chemistry sectors [1]. Great efforts have been devoted to the development of effective strategies to deal with the global challenge of CO$_2$ emission, including carbon capture and storage (CCS) [2], carbon capture and utilisation (CCU) [3], reducing fossil fuel consumption and boosting clean and renewable energy use [4]. Undoubtedly, CO$_2$ conversion and utilisation could be one of the attractive and sustainable solutions for the mitigation of CO$_2$ emissions, by turning CO$_2$ from a waste gas into an integral part of industrial processes. Various processes have been used to convert CO$_2$ into value-added fuels and chemicals, such as CO$_2$ reforming of CH$_4$ for hydrogen production, CO$_2$ hydrogenation for the synthesis of methanol, methane, formaldehyde, dimethyl ether, etc [5, 6]. Direct splitting of CO$_2$ into CO has also attracted great interest [7, 8], as CO is a useful chemical feedstock which can be used as a reactant to produce higher energy products. However, due to the high stability of CO$_2$, large amount of energy is required for the activation of CO$_2$ in the conventional CO$_2$ conversion process. For example, thermodynamic equilibrium calculation of CO$_2$ conversion shows that CO$_2$ begins to decompose into CO and O$_2$ near 2000 K with a very low conversion rate (< 1%). Reasonable conversion of CO$_2$ (~60%) can only be obtained at an extraordinary high temperature (3000-3500 K).

Non-thermal plasma technology has been considered as an attractive alternative to the conventional thermal or catalytic route for gas purification and energy conversion [9-14] due to its non-equilibrium character, low energy cost and unique ability to initiate both physical and chemical reactions at low temperatures [15, 16]. In a non-thermal plasma, the overall gas kinetic temperature remains low, while the electrons are highly energetic with a typical electron temperature of 1-10 eV, which can breakdown most chemical bonds of inert molecules (e.g. CO$_2$) and generate a large
number of reactive species for chemical reactions. The non-equilibrium character of such plasma could overcome thermodynamic barriers in chemical reactions (e.g. direct CO$_2$ decomposition) and enable thermodynamically unfavourable chemical reactions to occur at atmospheric pressure and low temperatures [15].

Up until now, several different types of plasma have been used for CO$_2$ conversion, including dielectric barrier discharges (DBDs), corona discharges, glow discharges, microwave discharges, radio frequency discharge and gliding arc discharges [17-28]. Most of previous works in this area mainly focused on the conversion of diluted CO$_2$ into CO and O$_2$. Inert gases such as He, Ar and N$_2$ were used as the dilution gases to assist CO$_2$ conversion [21]. Indarto et al investigated the effect of N$_2$, O$_2$, air and H$_2$O on the conversion of CO$_2$ in a gliding arc plasma reactor [27, 29]. Only N$_2$ was found to give a positive effect on CO$_2$ conversion. CO$_2$ conversion of 35% was achieved at a N$_2$ concentration 95% in the mixture feed gas, much higher than that in a pure CO$_2$ reaction (only 15-18%). However, the presence of N$_2$ in CO$_2$ reaction inevitably generates unwanted by-products such as NO$_x$. Similarly, Zheng et al reported that CO$_2$ conversion was much higher in the Ar system than that in the O$_2$ system in a DBD reactor [30]. To further improve the conversion of CO$_2$ and energy efficiency of the plasma process, different non-conductive materials have been introduced into the plasma system. Porous Al$_2$O$_3$ ($\alpha$-Al$_2$O$_3$ and $\gamma$-Al$_2$O$_3$) were packed into a pulsed corona discharge reactor for CO$_2$ conversion and $\gamma$-Al$_2$O$_3$ was found to enhance CO$_2$ conversion due to its high surface area and strong adsorption capability [31]. Yu et al investigated the decomposition of CO$_2$ in a packed bed DBD reactor using silica gel, quartz, $\alpha$-Al$_2$O$_3$, $\gamma$-Al$_2$O$_3$, CaTiO$_3$ as packing materials [32]. A series of Ca$_x$Sr$_{(1-x)}$TiO$_3$ with and without additive were used as a dielectric barrier for the splitting of CO$_2$ in a DBD reactor [33-35]. In their works, the high permittivity of the dielectrics led to an increasing in the plasma power with very dense and strong microdischarges, which significantly enhances the conversion of CO$_2$. These findings suggest that the interactions between plasma and packing materials play an important role in the plasma conversion of CO$_2$. However, a fundamental understanding of the interaction between plasma and packing materials
from both a physical and chemical perspective is still very patchy, especially the influence of packing materials on the physical characteristics (e.g. electric field, mean electron energy) of the discharge and consequent plasma chemical reactions is still not clear and has been paid less attention.

In this study, direct conversion of undiluted CO\textsubscript{2} into CO and O\textsubscript{2} is carried out in a cylindrical DBD reactor with and without packing at low temperatures. The effect of glass and BaTiO\textsubscript{3} beads on the physical characteristics of the discharge and chemical reaction performance is investigated to get a better understanding of plasma interactions with packing materials in CO\textsubscript{2} conversions.

2. Experimental

2.1 Experimental setup

The experiment is carried out in a cylindrical DBD reactor, as shown in figure 1. A 6 cm long stainless steel mesh is wrapped over a quartz tube with an external diameter of 25 mm and an inner diameter of 22 mm. A stainless steel rod with an outer diameter of 16 mm is placed in the centre of the quartz tube and acted as an inner electrode. As a result, the discharge gap is 3 mm with a discharge volume \( V \) of 10.1 ml. The inner electrode is connected to a high voltage output and the outer electrode is grounded via an external capacitor \( C_{\text{ext}} \) (0.47 \( \mu \text{F} \)). CO\textsubscript{2} is used as the feed gas without dilution and the flow rate is fixed at 50 ml/min. The DBD reactor is supplied by an AC high voltage power supply with a maximum peak voltage of 30 kV and a frequency of 5-20 kHz. The applied voltage \( (U_a) \) is measured by a high voltage probe (Testec, HVP-15HF), while the current \( (I_t) \) is recorded by a current monitor (Bergoz CT-E0.5). 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 (TDS2014). The discharge power is obtained by the area calculation of the \( Q-U \) Lissajous figure. Different packing materials (BaTiO\textsubscript{3} and glass beads) of 1 mm in diameter are fully packed into the discharge volume. In this case, the reactor can be
considered as a typical packed bed DBD system. For comparison, CO$_2$ conversion is also carried out in the DBD reactor with no packing. The gas temperature in the DBD reactor is measured by a fiber optic temperature probe (Omega, FOB102). The gas products are analysed by a two-channel gas chromatography (Shimadzu 2014) equipped with a flame ionisation detector (FID) and a thermal conductivity detector (TCD). The concentration of ozone is measured by an ozone monitor (2B, Model 106-M).

![Schematic diagram of the experimental setup](image)

**Figure 1.** Schematic diagram of the experimental setup

### 2.2 Parameter calculation

An equivalent electrical circuit model of the DBD reactor containing two capacitors in a series connection was described in our previous paper [16]. One of the capacitors $C_d$ represents the capacitance of the quartz tube and the other is the capacitance of the gap $C_{gap}$. The equivalent capacitance of the quartz tube $C_d$ is 96.58 pF, which is calculated according to the topology of a coaxial capacitor, as shown in Equation (1) [36]:

$$C_d = \frac{2 \pi \varepsilon_\circ \varepsilon l}{\ln\left(\frac{(d + x)}{d}\right)}$$  \hspace{1cm} (1)
where $\varepsilon_0$ is the dielectric constant of vacuum ($8.854 \times 10^{-12}$ F/m); $\varepsilon$ is the relative dielectric constant of quartz tube (3.70); $l$ is the discharge length; $d$ and $x$ are the inner diameter and wall thickness of the quartz tube, respectively, as shown in figure 2.

![Diagram of DBD reactor with no packing](image)

Figure 2. Transversal section of the DBD reactor with no packing

Figure 3 shows a typical $Q$-$U$ Lissajous figure for a DBD reactor. Lines BC and AD represent the discharge-off phase when there is only displacement current and their slopes correspond to the $C_{cell}$ in the plasma-off period. Lines AB and CD represent the discharge-on phase when the gas breakdown occurs in the gap and the plasma is ignited. The slope of Lines AB and CD is effective capacitance $C_{eff}$, which should equal $C_d$ for a fully bridged gap [37]. The detailed examination of the $Q$-$U$ plot and calculation for the capacitance of the gap $C_{gap}$ in the discharge-off phase, the charge $Q$ flowing through the DBD cell, the voltage on the dielectric materials $U_d$, the voltage across the gap $U_{gap}$ and the breakdown voltage $U_B$ can be found in our previous paper [16]. The peak-to-peak voltage ($Q_{pk-pk}$), charge discharged ($Q_d$) and charge transferred per half-cycle ($Q_{trans}$) can be obtained from the Lissajous figure, as plotted in figure 3 [38].
In the presence of packing pellets in the discharge gap, $C_{gap}$ represents the capacitance of gas-solid integration in the gas gap; and $U_{gap}$ is the sum of the voltage on the gas ($U_g$) and packing material ($U_p$). In this study, the beads are tightly packed into the discharge gap. The void fraction of the DBD reactor in the presence of packing materials is defined as $1 - V_p/V$ ($V_p$ is the total volume of packing beads), which is about 0.283 for the fully packing of glass or BaTiO$_3$ beads into the DBD reactor. To understand the effect of packing materials on the physical characteristics of the discharge, a simplified model has been established to determine the voltage across the gas and solid, respectively. The region of solid beads and gas is equivalently considered as two parallel plate capacitors, as shown in figure 4. The equivalent gap thicknesses in the gas ($d_g$) and solid ($d_p$) region are determined by equations (2) and (3):

$$d_g = \frac{2V_d \times \alpha}{\pi (D + d)}$$  \hspace{1cm} (2)$$

$$d_p = d_{gap} - d_g$$  \hspace{1cm} (3)$$

where $V_d$ is the discharge volume; $D$ is the outer diameter of the inner electrode.

The equivalent capacitances of the gas ($C_g$) and solid ($C_p$) regions are calculated in the form of a parallel plate capacitor:
\[ C_g = \frac{\varepsilon_g \cdot \varepsilon_0 \cdot S}{d_g} \]  
\[ C_p = \frac{\varepsilon_p \cdot \varepsilon_0 \cdot S}{d_p} \]  

where \( \varepsilon_g \) is the relative dielectric constant of CO\(_2\) (\( \varepsilon_g = 1.6 \)); \( \varepsilon_p \) is the relative dielectric constant of the packing materials (3.9 for glass bead and 10000 for BaTiO\(_3\)); \( S \) is the surface area of the outer electrode.

The gas voltage \( U_g \) can be obtained from the following equation:

\[ U_g = \frac{Q}{C_g} = \frac{U_p \cdot C_p}{C_g} = \frac{(U_{gap} - U_g) \cdot C_p}{C_g} \]  

Equation (6) can be rewritten in the following form by introducing equations (4) and (5):

\[ U_g = \frac{U_{gap}}{\frac{\varepsilon_g \cdot d_p + 1}{\varepsilon_p \cdot d_g}} \]  

Figure 4. Simplified model for the determination of the gas gap

To evaluate the performance of the plasma process, CO\(_2\) conversion, CO yield and selectivity are defined:
\[
\text{CO}_2 \text{ conversion (\%) } = \frac{\text{CO}_2 \text{ converted (mol/s)}}{\text{CO}_2 \text{ input (mol/s)}} \times 100
\]  
\tag{8}

\[
\text{CO yield (\%) } = \frac{\text{CO} \text{ formed (mol/s))}}{\text{CO}_2 \text{ input (mol/s)}} \times 100
\]  
\tag{9}

\[
\text{CO selectivity (\%) } = \frac{\text{CO} \text{ formed (mol/s))}}{\text{CO}_2 \text{ converted (mol/s)}} \times 100
\]  
\tag{10}

Specific energy density (SED) is defined as the ratio of the discharge power to the gas flow per unit volume:

\[
\text{SED (kJ/L)} = \frac{\text{Discharge power (W)}}{\text{CO}_2 \text{ flow rate (L/s)}}
\]  
\tag{11}

The energy efficiency of the plasma CO\textsubscript{2} conversion process is defined as the number of moles of CO\textsubscript{2} converted per unit of plasma power:

\[
E (\text{mmol/kJ}) = \frac{\text{CO}_2 \text{ converted (mol/s)}}{\text{Discharge power (W)}}
\]  
\tag{12}

3. Results and discussion

3.1 Effect of packed materials on discharge characteristics

Figure 5 presents the electrical signals of the CO\textsubscript{2} discharge with and without packing materials. In the discharge with no packing, a typical filamentary discharge can be clearly observed, which can also be confirmed by the numerous peaks in the current signal. In contrast, packing BaTiO\textsubscript{3} or glass beads into the entire discharge area generates a typical packed-bed effect and leads to a transition in the discharge behaviour from a filamentary discharge to a combination of surface discharge and filamentary discharge. The addition of BaTiO\textsubscript{3} or glass beads into the DBD reactor is found to significantly reduce the amplitude of the current peaks. In a packed-bed DBD reactor, filaments can only be generated in the small gap between the pellet-pellet and the pellet-quartz wall, while surface discharge can be formed on the surface of pellets near contact points between pellets. Similar findings were reported in our previous works where fully packing Ni/Al\textsubscript{2}O\textsubscript{3} or TiO\textsubscript{2} catalyst pellets into a DBD reactor significantly changes the discharge mode and inhibits the formation of
filamentary discharges due the decrease of the discharge volume [16, 39]. However, intense filamentary discharges were still formed when quartz wool was placed in the discharge area due to the porosity of this material and strong interactions between the plasma and quartz wool [15].

Note that the gap voltage of the CO₂ discharge in the packed bed DBD reactor is much lower than that of the discharge with no packing. The breakdown voltage \( U_B \) of the discharge significantly decreases from 3.43 kV without packing to 1.56 kV (packed with glass beads) and 1.03 kV (packed with BaTiO₃), respectively. This phenomenon can be ascribed to the reduced electrode gap and reduced pressure due to the packing of solid materials into the discharge gap. Such changes were also observed in previous studies where packing a series of materials (Ni/Al₂O₃, Al₂O₃, TiO₂, and zeolite 3A) into the discharge gap showed that the influence of dielectric constant of the packing materials on the reduction of breakdown voltage was weak [16, 40, 41].
Figure 5. Electrical signals of the CO$_2$ DBD: (a) with no packing; (b) packed with glass beads; (c) packed with BaTiO$_3$ beads (discharge power: 40W; feed flow rate: 50 ml/min; frequency: 9 kHz; SED: 48 kJ/L)

Figure 6 shows the Lissajous figures of the CO$_2$ discharge with and without packing material at the same discharge power of 40 W. The shape of the Lissajous figure changes from parallelogram to oval shape when either BaTiO$_3$ or glass beads are fully packed in the DBD reactor. This also indicates the change in the discharge characteristics. At the same discharge power, the applied voltage of the DBD increases from 14.1 kV$_{pk-pk}$ without packing to 15.3 kV$_{pk-pk}$ with the BaTiO$_3$
packing and 16.9 kV\textsubscript{pk-pk} with the glass beads packing, while the current in the discharge with no packing is much higher than that in the presence of packing beads, as shown in figure 5.

In the discharge-off phase, the total equivalent capacitance of the DBD reactor with no packing is about 13.6 pF. Adding the glass or BaTiO\textsubscript{3} beads to the plasma system significantly increases the value of this parameter to 43.8 pF and 54.4 pF, respectively. Similarly, the gap capacitance is also increased from 14.5 pF without packing to 80.2 pF and 124.6 pF when the discharge gap is fully packed with the glass or BaTiO\textsubscript{3} beads.

![Lissajous figures of the CO\textsubscript{2} DBD without and with different packing material at a constant discharge power of 40 W (feed flow rate: 50 ml/min; frequency: 9 kHz; SED: 48 kJ/L)](image)

Figure 6. Lissajous figures of the CO\textsubscript{2} DBD without and with different packing material at a constant discharge power of 40 W (feed flow rate: 50 ml/min; frequency: 9 kHz; SED: 48 kJ/L)

The influence of the packing solids on the effective capacitance of the DBD at different discharge powers is plotted in Figure 7. Increasing the discharge power or SED enhances the effective capacitance irrespective of the use of packing materials. For example, the effective capacitance of the discharge without packing increases from 25.5 pF to 58.6 pF when the discharge power varies from 20 W to 50 W. This can be clearly seen from the slope of the lines AB and CD in the Lissajous figure. In the discharge with no packing, the effective capacitance is much lower than the
capacitance of the quartz tube (96.58 pF). This phenomenon might be caused by the incomplete formation of microdischarge in the whole discharge gap under the experimental conditions. Similar observation was reported in a CH₄/CO₂ DBD [16]. In addition, it is also suggested that $C_{\text{eff}}$ depends on the spatial distribution of the discharge across the discharge gap over a half-period of the applied voltage. When the packing materials are placed in the reactor, the $C_{\text{eff}}$ increases compared with that of the discharge with no packing. Interestingly, the maximum $C_{\text{eff}}$ of 91.5 pF can be obtained when the BaTiO₃ beads are fully packed into the discharge gap at a discharge power of 40 W. This value is very close to the capacitance of the quartz tube. It is expected the effective capacitance should be equal to $C_d$ for a fully bridged gap [37]. This can demonstrate that the presence of BaTiO₃ beads in the discharge leads to the expansion of the discharge across the gap, and might consequently affect the plasma chemical reactions.

![Figure 7](image_url)

**Figure 7.** Effect of packing materials on the effective capacitance of the CO₂ discharge (feed flow rate: 50 ml/min; frequency: 9 kHz; SED: 24 – 60 kJ/L)

Figure 8 shows the influence of the packing materials on the charge characteristics of the CO₂ DBD at different discharge powers. It is found that the peak-to-peak charge increases with the increase in the discharge power. Both charge generated and transferred per half-cycle of the applied voltage
also increase with the discharge power. Similar evolution was observed in previous studies where these charge parameters increased with the discharge power in a plasma methane reforming process [16]. The addition of the packing materials to the DBD reactor has a significant effect on the charge characteristics of the CO₂ discharge. Both packing materials are found to bridge the gap between the electrodes and enhance the charge transfer between them.
Figure 8. Effect of packing materials on the charge generation and transfer in the pure CO$_2$ DBD: (a) peak-to-peak charge; (b) charge generated per half-cycle; (c) charge transferred per half-cycle (feed flow rate: 50 ml/min; frequency: 9 kHz; SED: 24 – 60 kJ/L)

3.2 Effect of packing materials on electric field and electron energy

The effect of the packing materials on the average electric field strength of the discharge at different discharge powers is shown in Figure 9. Clearly, increasing the discharge power effectively enhances the electric field of the CO$_2$ discharge regardless of the packing material used. The presence of the packing materials in the discharge also significantly improves the average electric field strength. The material (BaTiO$_3$) with a higher dielectric constant has a more significant effect on the electric field of the discharge. For example, the average electric field strength (25.01 kV/cm) in the DBD reactor fully packed with the BaTiO$_3$ beads is almost doubled compared to that of the discharge with no packing (12.90 kV/cm) at the same discharge power of 50 W. A similar finding was reported in [42] where the presence of TiO$_2$ pellets in a nitrogen DBD led to a significant increase of the electric field. Previous experimental [43, 44] and simulation studies [45, 46] showed that packing solid pellets especially the pellets with a high dielectric constant (e.g., BaTiO$_3$) into the discharge gap significantly enhanced the local electric field strength near contact points between the
pellets and the pellet – dielectric wall. The maximum local electric field near these contact points can be $10^{-4}$ times higher than that in the void in a plasma-catalysis system, depending on the properties of the packing materials such as contact angle, shape and dielectric constant, while the averaged electric field in an argon plasma fully packed with packing pellets was increased by a factor of 1.4 with increasing the dielectric constant of the packing materials from 10 to 1000, above this the change in the electric field became negligible [47]. Our results also show that the electric field of the CO$_2$ discharge is not a function of dielectric constant when the packing materials with different constants (3.9 and 10000) are fully packed in the DBD reactor. Table 1 presents the effect of the packing materials on the reduced electric field strength at different discharge powers. Similarly, increasing the plasma power significantly enhances the reduced electric field of the discharge, while the presence of the glass or BaTiO$_3$ beads in the plasma system leads to a higher reduced electric field.

![Figure 9. Effect of packing materials on the average electric field strength at different discharge powers (feed flow rate: 50 ml/min; frequency: 9 kHz; SED: 24 – 60 kJ/L)](image)
Table 1. Effect of packing materials on $E/N$ at different discharge powers

<table>
<thead>
<tr>
<th>Discharge power (W)</th>
<th>$E/N$ (Td) Without packing</th>
<th>$E/N$ (Td) Glass beads</th>
<th>$E/N$ (Td) BaTiO$_3$ beads</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>36.38</td>
<td>54.32</td>
<td>73.64</td>
</tr>
<tr>
<td>30</td>
<td>40.54</td>
<td>58.50</td>
<td>79.07</td>
</tr>
<tr>
<td>40</td>
<td>46.02</td>
<td>62.30</td>
<td>86.04</td>
</tr>
<tr>
<td>50</td>
<td>47.99</td>
<td>67.62</td>
<td>93.02</td>
</tr>
</tbody>
</table>

The electron energy distribution function (EEDF) of the CO$_2$ discharge under our experimental conditions is calculated by BOLSIG+ [48]. Figure 10 shows the mean electron energy as a function of the reduced electric field ($E/N$). The effect of the packing solids on the mean electron energy of the discharge has also been investigated, as shown in figure 11. Clearly, increasing the plasma power or SED leads to generate more electrons with higher energy. Packing the BaTiO$_3$ pellets in the discharge gap almost doubles the mean electron energy at the discharge power of 50 W, while the mean electron energy of the discharge with glass beads is increased by around 46.23%. In our previous study, we reported that the integration of plasma and TiO$_2$ strongly affected the electron energy distribution in a N$_2$ discharge with an increase in both highly energetic electrons and electric field strength [39]. These results suggest that the presence of solid pellets in the discharge gap play a crucial role in inducing physical effects, such as the enhancement of electric field and mean electron energy, which in turn produces more energetic electrons and chemically reactive species for plasma reactions and consequently contributes to the conversion of CO$_2$. 
3.3 Effect of packing materials on CO₂ conversion

Plasma conversion of CO₂ is carried out in the DBD reactor with and without packing material. CO₂ conversion increases with the increase of the discharge power, as shown in figure 12. Our calculation has shown that increasing the plasma power or SED effectively enhance the average electric field and mean electron energy in the discharge, all of which can generate more energetic...
electrons and reactive species for plasma chemical reaction, consequently improves the conversion of CO$_2$. The presence of the packing materials in the discharge gap makes the reactor more effective for CO$_2$ conversion, even though fully packing these packing beads into the discharge gap significantly decreases the residence time of CO$_2$ molecules in the discharge area from 12.89 s with no packing to 3.65 s with packing. It is worth noting that plasma-induced adsorption and desorption of CO$_2$ on the BaTiO$_3$ surface may prolong the retention time of CO$_2$ in the discharge and partly compensate the reduced of CO$_2$ residence time due to the decrease of the discharge volume. Compared to the plasma reaction with no packing, the addition of BaTiO$_3$ and glass beads to the plasma system increases the conversion of CO$_2$ by around 75% and 35%, respectively. It is found that the conversion of CO$_2$ is not a function of dielectric constant when the packing pellets with different dielectric constants are placed in the plasma reactor. The enhancement of CO$_2$ conversion is mainly attributed to the changes in the discharge characteristics, such as the increase of the average electric field and mean electron energy when solid pellets are packed into the discharge volume, as shown in figures 9 and 11. However, with the BaTiO$_3$ packing, the contribution of plasma photocatalytic surface reaction to the enhancement of CO$_2$ conversion cannot be ruled out [49]. It is believed that plasma discharges can generate strong UV radiation without using extra UV sources (e.g. UV lamps) to activate photocatalysts such as BaTiO$_3$. Nevertheless, the contribution of this mechanism to the photocatalytic reactions is still not clear. Previous works reported that UV radiation generated by plasma discharges is not always the controlling factor to activate photocatalysts [50, 51]. In contrast, the electrons with a high energy (> 3.0 eV for BaTiO$_3$) generated by the CO$_2$ discharge can trigger electron impact activation of BaTiO$_3$ photocatalysts to form electron-hole pairs, which contributes to the enhanced conversion of CO$_2$. 
Figure 12. Effect of packing materials on CO₂ conversion (feed flow rate: 50 ml/min; frequency: 9 kHz; SED: 24 – 60 kJ/L)

Figure 13 shows the effect of the packing materials on the energy efficiency of the plasma processing of CO₂ as a function of the discharge power. Compared to the plasma reaction with no packing, the presence of BaTiO₃ and glass beads in the gas gap significantly enhances the energy efficiency of the plasma process. Packing the BaTiO₃ into the discharge leads to an increase in the energy efficiency of the process by 75% compared to the reaction with no packing at the same discharge power of 50 W. The maximum energy efficiency of 0.254 mmol/kJ is achieved when the BaTiO₃ pellets are fully packed into the discharge volume at a discharge power of 20 W and a feed flow rate of 50 ml/min. Figure 14 shows a comparison of the energy efficiency for CO₂ conversion using DBDs with and without packing. It is clear that there is a balance between the maximum CO₂ conversion and maximum energy efficiency of the process. Further optimisation of the plasma reactor geometry, feed conditions, different packing methods, and packing materials especially the use of suitable catalysts would be expected to improve the energy efficiency of the process with a high CO₂ conversion.
Figure 13. Effect of discharge power on energy efficiency (feed flow rate: 50 ml/min; frequency: 9 kHz; SED: 24 – 60 kJ/L)

Figure 14. Comparison of energy efficiency for CO$_2$ conversion with different DBD reactors

The influence of the packing solids on CO selectivity and CO yield at different discharge powers is plotted in figure 15. CO selectivity is almost independent of the discharge power and packing materials, while CO yield increases with the increase of the discharge power. The presence of the BaTiO$_3$ in the discharge gap significantly enhances the yield of CO by 72.94%. The selectivity of CO based on carbon atom (equation 10) is close to 100%, which suggests that stoichiometric
conversion of CO₂ to CO is achieved in this study. This can be confirmed by the linear relationship between the CO₂ conversion and CO yield (see figure 16), which suggests that the production of CO mainly comes from the dissociation of CO₂. The electron impact dissociation of CO₂ will most likely result in CO in its ground state (^1Σ) and O atoms in both the ground state (^3P) and the metastable state (^1D). However, previous work reported that CO can also be formed in excited state since CO bands were observed [15]. The stoichiometric conversion of CO₂ to CO can be further demonstrated by the fact that no carbon deposition and ozone are detected in the plasma reactions. In contrast, Horvath et al found that CO and ozone were the main gas products in the decomposition of pure CO₂ by a corona discharge [20]. Mikoviny et al reported that adding trace oxygen into pure CO₂ significantly increased the concentration of ozone and CO in the CO₂ splitting using a negative corona discharge reactor [19].
4. Conclusions

Plasma-assisted conversion of undiluted CO$_2$ into CO and O$_2$ has been carried out in a cylindrical DBD reactor with and without packing materials. The influence of the packing materials (BaTiO$_3$
and glass beads) on the CO₂ discharge characteristics and CO₂ conversion has been investigated. The presence of BaTiO₃ and glass beads in the DBD reactor changes the discharge behaviour and shows a transition from a typical filamentary discharge with no packing to a combination of filamentary discharge and surface discharge at the same discharge power. The addition of BaTiO₃ into the plasma system significantly enhances the average electric field and mean electron energy by 93.87% and 98.49%, respectively, which also affects the plasma chemical reactions. The use of packing materials (BaTiO₃ and glass beads) in the discharge gap is found to make the DBD reactor more effective for CO₂ conversion even though the residence time of CO₂ in the discharge is reduced due to the decrease of the discharge volume at the same gas flow rate. Compared to the plasma CO₂ conversion with no packing, the presence of BaTiO₃ beads in the DBD reactor significantly increases the conversion of CO₂ by 75%. These results indicate that the change of the discharge properties (e.g. electric field and mean electron energy) significantly enhances CO₂ conversion, CO yield and energy efficiency of the plasma process. In addition, highly energetic electrons (> 3.0 eV) generated by the discharge could activate photocatalyst (BaTiO₃) to form electron-hole pairs on the surface of BaTiO₃, which also contributes to the enhanced conversion of CO₂.

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