Plasma-photocatalytic conversion of CO$_2$ at low temperatures: Understanding the synergistic effect of plasma-catalysis

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A coaxial dielectric barrier discharge (DBD) reactor has been developed for plasma-catalytic conversion of CO$_2$ into value-added chemicals at low temperatures (<150 °C) and atmospheric pressure. The effect of specific energy density (SED) on the performance of the plasma process has been investigated. In the absence of a catalyst in the plasma, the maximum conversion of CO$_2$ reaches 21.7 %. The synergistic effect from the combination of plasma with photocatalysts (BaTiO$_3$ and TiO$_2$) at low temperatures contributes to a significant enhancement of both CO$_2$ conversion and energy efficiency by up to 250%. The synergy of plasma-catalysis for CO$_2$ conversion can be attributed to both the physical effect induced by the presence of catalyst pellets in the discharge and the photocatalytic surface reaction driven by the plasma.

Introduction

Recently, the abatement of carbon dioxide (CO$_2$) has become a major global challenge as CO$_2$ is the main greenhouse gas and its emissions lead to the problems of climate change and global warming. Different strategies are being developed to tackle the challenges associated with CO$_2$ emissions, including carbon capture and storage (CCS), carbon capture and utilization (CCU), reducing fossil fuel consumption and boosting clean and renewable energy use. Direct conversion of CO$_2$ into value-added fuels and chemicals (e.g., CO, CH$_4$, and methanol) offers an attractive route for efficient utilisation of low value CO$_2$ whilst significantly reducing CO$_2$ emissions. However, CO$_2$ is a highly stable and non-combustible molecule, requiring considerable energy for upgrading and activation. Various synthetic approaches for CO$_2$ conversion have been explored, including solar driven photochemical reduction, electrochemical reduction and thermal catalysis. Despite their potential, further investigation into the development of cost-effective H$_2$ production methods, novel multifunctional catalysts and new catalytic processes are essential to improve the overall energy efficiency of CO$_2$ conversion processes and the product selectivity to practical and implementable levels.

Cold plasma technology provides a promising alternative to the traditional catalytic route for the conversion of CO$_2$ into value-added fuels and chemicals at ambient conditions. In cold plasmas, highly energetic electrons and chemically reactive species (e.g., free radicals, excited atoms, ions, and molecules) can be generated for the initiation of both physical and chemical reactions. Cold plasma has a distinct non-equilibrium character, which means the gas temperature in the plasma can be close to room temperature, whilst the electrons are highly energetic with a typical mean energy of 1-10 eV. As a result, cold plasma can easily break most chemical bonds (e.g., C-O bonds), hence overcoming the disadvantage of high temperature required by thermal catalysis, and enable thermodynamically unfavorable chemical reactions (e.g., CO$_2$ decomposition) to occur at ambient conditions. However, the use of plasma alone leads to low selectivity and yield towards the target end-products. Recently, the combination of plasma with catalysis, known as plasma-catalysis, has attracted tremendous interest for the destruction of gas pollutants in waste gas streams and fuel production from methane and hydrocarbons. The integration of plasma and solid catalysts has great potential to generate a synergistic effect, which can activate the catalysts at low temperatures and improve their activity and stability, resulting in the remarkable enhancement of reactant conversion, selectivity and yield of target products, as well as the energy efficiency of the plasma process. Direct conversion of CO$_2$ into valuable CO and O$_2$ has been explored using different cold plasmas. However, most previous works have mainly focused on the conversion of CO$_2$ diluted with noble gases (e.g., He and Ar), which is not preferable from an industrial application point of view. Further fundamental work is still required to optimise and improve the energy efficiency of the plasma process. In addition, finding a suitable and cost-effective catalyst for this reaction to enhance the efficiency of the process is a great challenge. A detailed understanding of the synergistic effect resulting from the combination of plasma and catalysts at low temperature is still required due to gaps in current knowledge.

In this work, a coaxial dielectric barrier discharge (DBD) has been developed for the plasma-photocatalytic reduction of CO$_2$ into CO and oxygen at low temperature. The synergistic effect resulting from the combination of plasma and photocatalysts (BaTiO$_3$ and TiO$_2$) has been investigated from both physical and chemical perspectives.

Experimental

In this study, a coaxial dielectric barrier discharge (DBD) reactor has been developed for the plasma-catalytic reduction of pure CO$_2$ into higher value chemicals at atmospheric pressure and low temperatures (< 150 °C), as shown in Fig. 1. An Al foil (ground electrode) was wrapped around the outside of a quartz tube with an external diameter of 22 mm and an inner diameter of 19 mm. A stainless steel tube with an outer diameter of 14 mm was used as the inner electrode (high voltage electrode). The discharge gap was fixed at 2.5 mm, whilst the discharge length was varied from 90 to 150 mm. CO$_2$ was used as the feed gas without dilution at a flow rate of 15-60 ml/min. The DBD reactor was supplied by an AC high voltage power supply with a peak-to-peak voltage of 10 kV and a frequency of 50 Hz. All the electrical signals were sampled by a four-channel digital oscilloscope (TDS2014). Different
catalyst pellets BaTiO$_3$ (TCU) and TiO$_2$ (Alfa Aesar) with a diameter of 1 mm were packed into the discharge gap along the bottom of the quartz tube. Our previous work demonstrated that this packing method induces effective plasma-catalyst interactions, which might generate a synergistic effect and hence promote plasma-catalytic chemical reactions$^6$. The temperature in the DBD reactor was measured by a fiber optic temperature probe (Omega, FOB102). X-ray diffraction (XRD) patterns of the fresh catalyst samples were recorded by a Siemens D5000 diffractometer using Cu-Kα radiation in the 2θ range between 10° and 70°. X-ray photoelectron spectroscopic (XPS) measurements were carried out on a Perkin-Elmer PHI-5400 XPS system with mono-chromatic Mg Kα (1253.6 eV) X-rays with a data acquisition system. The spectra are referenced to C1s peak at 284.5 eV. The gas products were 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 was measured by an ozone monitor (2B, Model 106-M). To evaluate the performance of the plasma process, the specific energy density (SED), CO$_2$ conversion ($C_{CO_2}$) and energy efficiency (E) are defined as follows:

$$\text{SED (kJ/L)} = \frac{\text{Discharge power (kW)}}{\text{CO}_2 \text{ flow rate (L/s)}}$$  \hspace{1cm} (1)  

$$C_{CO_2} (%) = \frac{\text{CO}_2 \text{ converted (mol/s)}}{\text{CO}_2 \text{ input (mol/s)}} \times 100$$  \hspace{1cm} (2)  

$$E (\text{mmol/kJ}) = \frac{\text{CO}_2 \text{ converted (mol/s)}}{\text{Discharge power (kW)}}$$  \hspace{1cm} (3)  

Results and discussion

Plasma-assisted conversion of CO$_2$ without catalyst

Fig. 2 shows the effect of specific energy density (SED) on the conversion of CO$_2$ and the energy efficiency of the plasma reaction in the absence of a catalyst. Clearly, increasing the specific energy density significantly enhances CO$_2$ conversion due to the increase in energy input to the discharge. The conversion of CO$_2$ is increased by a factor of 3 (from 6.65% to 21.72%) as the SED rises from 8 kJ/L to 80 kJ/L. Similar conversion trends have been reported either using cold plasma alone or using plasma-catalysis for chemical reactions$^{23, 24}$. Our previous works have shown that increasing discharge power at a constant frequency could effectively enhance the electric field, electron density and gas temperature in the discharge$^{25-27}$, all of which may contribute in different ways to the improvement in conversion. Moreover, the increase in discharge power produces more chemically reactive species (e.g. O atoms), which can further induce CO$_2$ dissociation to enhance its conversion. A lower feed gas flow rate was reported to be beneficial for improving the conversion of reactants due to longer retention time of the reactants in the plasma. In contrast, the specific energy density has an opposite effect on the energy efficiency of the plasma process. Increasing the SED from 8 kJ/L to 80 kJ/L leads to a decrease of the energy efficiency from 0.37 mmol/kJ to 0.12 mmol/kJ, which is consistent with previous results$^{28}$. In this work, the maximum energy efficiency of 0.37 mmol/kJ is achieved at the lowest specific energy density of 8 kJ/L with a discharge power of 8 W, a CO$_2$ feed flow rate of 60 mL/min and a discharge length of 150 mm.

CO$_2$ dissociation by electron impact vibrational excitation (Eqs 4-5) is believed to be the most effective pathway for CO$_2$ conversion in cold plasmas, which can lead to a high energy efficiency of more than 60%$^{29}$:

$$e + CO_2 \rightarrow e + CO_2 (v')$$  \hspace{1cm} (4)  

$$e + CO_2 (v') \rightarrow e + CO + O$$  \hspace{1cm} (5)
WHERE $v^*$ IS THE VIBRATIONAL EXCITED STATE. UP TO 97% OF THE TOTAL PLASMA ENERGY CAN BE TRANSFERRED FROM ELECTRONS TO 

VIBRATIONAL EXCITATION OF $\text{CO}_2$ IF THE PLASMA DISCHARGES HAVE AN ELECTRON TEMPERATURE OF 1–2 eV, OR A REDUCED ELECTRIC FIELD (E/N) OF 20–40 Td. RECENT PLASMA MODELLING OF $\text{CO}_2$ SPLITTING BY A DBD SHOWN THAT AT A HIGH REDUCED ELECTRIC FIELD (E/N = 150-200 Td), ONLY 12% OF THE ENERGY CAN BE ALLOCATED TO VIBRATIONAL STATES, WHEREAS ~79% GOES TO ELECTRONIC EXCITED STATES, AND ~4% AND ~5% CAN BE TRANSFERRED TO DISSOCIATION AND IONIZATION OF $\text{CO}_2$, RESPECTIVELY. THEIR RESULTS SHOWED THAT THE MAJORITY (94%) OF $\text{CO}_2$ CONVERSION IS INDUCED BY REACTIONS (E.G. DISSOCIATION) WITH GROUND STATE $\text{CO}_2$ (SHOWN IN EQ. 6) AND ONLY 6% OF $\text{CO}_2$ CONVERSION IS BY REACTIONS WITH VIBRATIONAL EXCITED $\text{CO}_2$ AT A HIGH ELECTRIC FIELD.

$e + \text{CO}_2 \rightarrow e + \text{CO} + O$  \hspace{1cm} (6)

THE ELECTRON IMPACT DISSOCIATION OF $\text{CO}_2$ IN ITS VIBRATIONAL EXCITED STATES (EQ. 5) OR GROUND STATE (EQ. 6) WILL MOST LIKELY RESULT IN $\text{CO}$ IN ITS GROUND STATE ($^1\Sigma$) AND O ATOMS IN BOTH THE GROUND STATE ($^3\text{P}$) AND METASTABLE STATE ($^1\text{D}$). HOWEVER, SINCE $\text{CO}$ BANDS WERE OBSERVED IN THE EMISSION SPECTRA OF THE $\text{CO}_2$ DBD, $\text{CO}$ COULD ALSO BE FORMED IN EXCITED STATES.

IN THIS STUDY, THE AVERAGE ELECTRIC FIELD AND MEAN ELECTRON ENERGY OF THE PLASMA UNDER OUR EXPERIMENTAL CONDITIONS WITHOUT A CATALYST IS AROUND 1.75 kV/mm AND 1.5 eV, OBTAINED FROM LISSAJOU FIGURE AND BOLSIG$^2$ CODE BASED ON ELECTRON ENERGY DISTRIBUTION FUNCTION (EEDF), RESPECTIVELY. THIS SUGGTS THAT THE ELECTRON IMPACT VIBRATIONAL EXCITATION OF $\text{CO}_2$ MIGHT PLAY A DOMINANT ROLE IN $\text{CO}_2$ CONVERSION IN OUR EXPERIMENTS.

OXYGEN CAN BE FORMED FROM THE THREE-BODY RECOMBINATION OF ATOMIC OXYGEN (EQ. 7) OR FROM THE REACTION WITH A GROUND STATE $\text{CO}_2$ MOLECULE (EQ. 8).

$O + O + M \rightarrow O_2 + M$  \hspace{1cm} (7)

$O + \text{CO}_2 \rightarrow \text{CO} + O_2$  \hspace{1cm} (8)

OXYGEN MIGHT ALSO BE GENERATED DIRECTLY BY ELECTRON IMPACT DISSOCIATION OF $\text{CO}_2$ IF THE ELECTRON HAS A HIGH ENERGY (> 15 eV).

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\[ e + CO_2 \rightarrow C + O_2 + e \quad (9) \]

In this study, no carbon deposition is observed after the plasma conversion of CO\(_2\) with and without catalyst. Ozone could be formed by the following reaction:

\[ O + O_2 + M \rightarrow O_3 + M \quad (10) \]

However, ozone was not detected in this work. This agrees with recent modelling work in which CO and O\(_2\) were identified as the main products and the calculated fractional density of O\(_3\) was only 0.05%-30. The maximum rate for ozone formation in a DBD is two orders of magnitude lower than that of the three-body recombination of atomic oxygen for O\(_2\) production30. Our previous study has shown the formation of CO and CO\(_2\) spectra in a similar dielectric barrier discharge containing CO\(_2\) using optical emission spectroscopic diagnostics6, which suggests electron impact ionisation of CO\(_2\) occurs in the plasma CO\(_2\) reaction.

\[ e + CO_2 \rightarrow e + e + CO_2^* \quad (11) \]

**Plasma-photocatalytic conversion of CO\(_2\)**

The effect of BaTiO\(_3\) and TiO\(_2\) photocatalysts on the conversion of CO\(_2\) is shown in Fig. 3. It is clear that the presence of both BaTiO\(_3\) and TiO\(_2\) in the discharge significantly enhances the CO\(_2\) conversion and energy efficiency of the plasma process. Packing BaTiO\(_3\) pellets into the discharge gap exhibits exceptional performance with a remarkable enhancement of both CO\(_2\) conversion (from 15.23% to 38.30%) and energy efficiency (from 0.24 mmol/kJ to 0.60 mmol/kJ) by a factor of 2.5 at a SED of 28 kJ/L. To understand the role of plasma in the reaction, a purely thermal experiment has been carried out by heating both photocatalysts in a pure CO\(_2\) flow at 150 °C. No conversion and adsorption of CO\(_2\) is observed. Thermodynamic equilibrium calculation of the CO\(_2\) reaction has also confirmed that the conversion of CO\(_2\) is almost zero at low temperatures (e.g., 150 °C), suggesting that an extremely low CO\(_2\) conversion is expected from the thermal catalytic reduction of CO\(_2\) when carried out at the same temperature as that used in the plasma reaction (see Fig. S11 in the Supporting Information). The results clearly show that the exceptional reaction performance has been achieved by the use of plasma-catalysis, which is much higher than the sum of plasma-alone and catalysis alone, indicating the formation of a synergistic effect when combining plasma with photocatalysts at low temperatures.

Catalysts can be integrated into a DBD system in different ways. The presence of the catalyst pellets in part of the gas gap still shows predominantly filamentary discharges and surface discharges on the catalyst surface, which induces effective interactions between plasma and catalyst for CO\(_2\) activation. In this work, the dielectric constant of BaTiO\(_3\) and TiO\(_2\) is 10000 and 85, respectively. Previous experimental32, 33 and simulation34, 35 studies have shown that packing catalyst pellets, especially pellets with a high dielectric constant (e.g., BaTiO\(_3\)), into the discharge gap can generate a non-uniform electric field with enhanced 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 much higher than that in the void in a plasma-catalysis reactor, depending on the contact angle, curvature and dielectric constant of the materials36. The space (including the space filled with pellets) averaged electric field in a plasma fully packed with packing pellets is initially increased by a factor of 1.4 when increasing the dielectric constant of the materials from 10 to 1000, above this the change in the electric field becomes negligible36. We have reported that the interaction of plasma and TiO\(_2\) exhibited a strong effect on the electron energy distribution in the discharge with an increase in both highly energetic electrons and electric field36. This phenomenon can also be confirmed by previous work, showing that the presence of TiO\(_2\) in a plasma leads to a significant increase of the reduced electric field37. These results suggest that the presence of the catalyst pellets in the plasma gap play a crucial role in inducing physical effects, such as enhancement of the electric field and production of more energetic electrons and reactive species, which in turn leads to chemical effects and contributes to the conversion of CO\(_2\). In this study, the electric field is increased by 9.0% and 10.9% with the presence of TiO\(_2\) and BaTiO\(_3\) in the discharge gap, respectively; whilst the corresponding mean electron energy is increased by 10.8% and 13.4% (see Fig. S12 in the Supporting Information). Both of these effects contribute to the enhancement of the CO\(_2\) conversion.

However, the enhancement of the reaction performance in terms of CO\(_2\) conversion and energy efficiency is found to be more significant than only due to the changes in plasma physical parameters (e.g. average electric field). This suggests that in addition to the plasma physical effect and the resulting gas phase reactions (Eqs. 4-11), the contribution of a plasma-activated photocatalytic reaction to the synergy of plasma-catalysis cannot be ruled out. The XRD patterns of the samples show that BaTiO\(_3\) has the tetragonal phase, while TiO\(_2\) exhibits the crystal structure of anatase (see Fig. S13 in the Supporting Information). TiO\(_2\) is a widely used photocatalyst with a wide band gap of 3.2 eV for anatase phase, while BaTiO\(_3\) is a perovskite semiconductor photocatalyst with a band gap of 2.8-3.0 eV for tetragonal phase. It is well known that photocatalysts can be activated through the formation of electron-hole (e\(^{-}\)-h\(^{+}\)) pairs with the aid of sufficient photonic energy (h\(_{\nu}\)) with an appropriate wavelength to overcome the band-gap between the valence band and the conductive band38:

\[ \text{TiO}_2 + h\nu \rightarrow e^{-} + h^{+} \quad (12) \]

\[ \text{BaTiO}_3 + h\nu \rightarrow e^{-} + h^{+} \quad (13) \]

Plasma discharges can generate UV radiation without using any extra UV sources (e.g. UV lamps). This has been confirmed by the dominated N\(_2\) (C-B) bands (between 300 nm and 400 nm) in a CO\(_2\) DBD in our previous work6, 39. However, UV radiation
generated by plasma discharges is not always the controlling factor to activate photocatalysts\cite{40}. Whitehead has suggested that electron-hole pairs can be created by electron impact upon the surface of photocatalysts since DBD can generate electrons of very similar energy (3 - 4 eV) to the photons\cite{13,41}, as shown in Eqs. 14-15. Nakamura et al have also reported that photocatalysts can be activated by plasma and the electrons can be trapped onto the formed oxygen vacancies (V\textsubscript{o}) to enhance the photoexcitation process\cite{42}. In this study, the highly energetic electrons generated by plasma are considered the main driving force to activate the photocatalysts for CO\textsubscript{2} conversion.

\begin{align}
\text{TiO}_2 + e^- (>3.2 \text{ eV}) &\rightarrow e^- + h^+ \quad (14) \\
\text{BaTiO}_3 + e^- (>3.0 \text{ eV}) &\rightarrow e^- + h^+ \quad (15)
\end{align}

Previous investigation has shown that the photocatalytic conversion of CO\textsubscript{2} is a multistep process, which involves the adsorption and subsequent activation of CO\textsubscript{2} molecules on the surface of photocatalysts and the dissociation of the C-O bond. The key step is the activation of CO\textsubscript{2} molecules through the transfer of trapped electrons to adsorbed CO\textsubscript{2} molecules in the V\textsubscript{o}\cite{43}. In this study, the highly energetic electrons generated by plasma are considered the main driving force to activate the photocatalysts for CO\textsubscript{2} conversion.

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However, the recombination rate of electron-hole pairs is 2 or 3 orders of magnitude faster than that of charge separation and transfer in a defect-free photocatalyst, which will limit the efficiency of CO\textsubscript{2} conversion\cite{43}. The defect disorders in photocatalysts, such as V\textsubscript{o}, play an important role in the CO\textsubscript{2} reduction processes. V\textsubscript{o} has been considered as the active site for the adsorption and activation of reactants in a photocatalytic reaction\cite{44}. In this study, XPS measurement has been performed to investigate the surface structure and element valence of the photocatalysts. Fig. 4(a) shows the deconvolution spectra of Ti 2p in the BaTiO\textsubscript{3} sample. Two components (Ti 2p\textsubscript{3/2} and Ti 2p\textsubscript{1/2}) are identified and can be deconvoluted into 4 peaks. Two peaks at higher binding energy (459.88 and 465.57 eV) are assigned to the formal valence of Ti (4+) in BaTiO\textsubscript{3}; whilst the Ti 2p\textsubscript{3/2} and Ti 2p\textsubscript{1/2} peaks of Ti\textsuperscript{3+} are located at around 457.85 eV and 463.67 eV. The presence of Ti\textsuperscript{3+} in the BaTiO\textsubscript{3} sample demonstrates the formation of V\textsubscript{o} on the catalyst surface through the following reaction\cite{45,46}:

\begin{align}
2\text{Ti}^{4+} + \text{O}^2^- &\rightarrow \text{V}_o + 2\text{Ti}^{3+} + 1/2 \text{O}_2 
\end{align}

where O\textsuperscript{2-} is the lattice oxygen. Clearly, the formation of V\textsubscript{o} is followed by the change in the oxidative state of the vicinal Ti from Ti\textsuperscript{4+} to Ti\textsuperscript{3+} to retain the balance of local charge. Similarly, the Ti 2p\textsubscript{3/2} and Ti 2p\textsubscript{1/2} peaks of Ti\textsuperscript{3+} can also be detected in the XPS profile of TiO\textsubscript{2}, as shown in Fig. 4(b). We find that there are more Ti\textsuperscript{3+} species in the BaTiO\textsubscript{3} (60.86%) sample than in the TiO\textsubscript{2} (49.89%), which suggests more active sites (V\textsubscript{o}) were formed in the BaTiO\textsubscript{3} catalyst, resulting in the higher CO\textsubscript{2} conversion using the BaTiO\textsubscript{3} catalyst.
Moreover, the combination rate of electron-hole pairs can also be significantly reduced in a plasma-photocatalytic system due to the presence of the electric field and the interactions between the plasma and photocatalyst. In this study, the process of plasma-photocatalytic conversion of CO$_2$ can be described by Fig. 5. The electron (e$^-$) - hole (h$^+$) pairs are generated with the aid of highly energetic electrons from the gas discharge, and are moved in the opposite direction by the electric field. In the electron transfer process, CO$_2$ adsorbed in the V$_o$ is reduced to the anion radical CO$_2$$^-$ by electrons (Eq.17), followed by the decomposition of CO$_2$$^-$ into CO and the occupation of one oxygen atom in the V$_o$ site. The overall reaction is expressed in Eq.18, in which [Photocatalyst + V$_o$] and [Photocatalyst] represent the defective and defect-free photocatalysts, respectively.

$$\text{CO}_2 + e^- \rightarrow \text{CO}_2^-$$  \hspace{1cm} (17)
$$\text{CO}_2 + [\text{Photocatalyst} + V_o] \rightarrow \text{CO} + [\text{Photocatalyst}]$$  \hspace{1cm} (18)
$$4h^+ + 2O_2^- \rightarrow O_2$$  \hspace{1cm} (19)
$$e^- + Ti^{4+} \rightarrow Ti^{3+}$$  \hspace{1cm} (20)

In addition, V$_o$ can be regenerated by oxidising the surface O$_2$ anions using holes, followed by releasing O$_2$, as shown in Eq. 19. To balance the charge, the Ti$^{4+}$ in the vicinity of the regenerated V$_o$ can be reduced to Ti$^{3+}$ by electrons $^{43,49,50}$. This cyclic healed-regeneration of the oxygen vacancies maintains the equilibrium of the active sites in the photocatalysts and controls the conversion of CO$_2$, which can be confirmed by our experimental results as the CO$_2$ conversion did not change significantly when the plasma discharge was on for nearly two hours.

Therefore, we find that the synergistic effect resulting from the integration of DBD and photocatalysis for CO$_2$ conversion at low temperatures (without extra heating) can be attributed to both the physical effect induced by the presence of photocatalysts in the discharge and the photocatalytic surface reaction driven by the discharge.
Energy efficiency

Fig. 6 shows a comparison of the energy efficiency for CO$_2$ conversion with different plasma processes. It is clear that the energy efficiency of the plasma CO$_2$ conversion in the presence of catalysts in this work is much higher than previous results. The combination of DBD and photocatalysts leads to a significant enhancement in CO$_2$ conversion and energy efficiency of the plasma process. Previous simulation work has suggested that the energy efficiency of a plasma reactor can be enhanced by a factor of 4 when using rectangular pulses instead of a sinusoidal voltage. Further improvement in the energy efficiency for this process can be expected from the optimisation of the plasma power and the design of new catalysts (e.g. coating metal nanoparticles on the photocatalysts).

Conclusions

In this study, plasma-photocatalytic conversion of CO$_2$ into CO and O$_2$ has been investigated using a DBD reactor combined with BaTiO$_3$ and TiO$_2$ catalysts. The combination of plasma with BaTiO$_3$ and TiO$_2$ catalysts has shown a synergistic effect, which significantly enhances the conversion of CO$_2$ and the energy efficiency by a factor of 2.5 compared to the plasma reaction in the absence of a catalyst. The presence of the catalyst pellets in the plasma gap is found to play a dominant role in inducing plasma physical effects, such as the enhancement of the electric field and production of more energetic electrons and reactive species, which in turn leads to chemical effects and contributes to the conversion of CO$_2$. The overall synergistic effect resulting from the integration of DBD with photocatalysis for CO$_2$ conversion at low temperatures (without extra heating) can be attributed to both the physical effect induced by the presence of the catalyst in the discharge and the photocatalytic surface reaction driven by the discharge.

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Notes and references
