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Plasma-photocatalytic conversion of CO₂ 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 CO₂ 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 CO₂ reaches 21.7 %. The synergistic effect from the combination of plasma with photocatalysts (BaTiO₃ and TiO₂) at low temperatures contributes to a significant enhancement of both CO₂ conversion and energy efficiency by up to 250%. The synergy of plasma-catalysis for CO₂ 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 (CO₂) has become a major global challenge as CO₂ 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 CO₂ 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 CO₂ into value-added fuels and chemicals (e.g., CO, CH₄, and methanol) offers an attractive route for efficient utilisation of low value CO₂ whilst significantly reducing CO₂ emissions¹. However, CO₂ is a highly stable and non-combustible molecule, requiring considerable energy for upgrading and activation. Various synthetic approaches for CO₂ conversion have been explored, including solar driven photochemical reduction², electrochemical reduction³ and thermal catalysis⁴. Despite their potential, further investigation into the development of cost-effective H₂ production methods, novel multifunctional catalysts and new catalytic processes are essential to improve the overall energy efficiency of CO₂ 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 CO₂ into value-added fuels and chemicals at ambient conditions⁵. 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 eV⁶. 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. CO₂ 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 hydrocarbons⁶⁻¹³. 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 process⁶. Direct conversion of CO₂ into valuable CO and O₂ has been explored using different cold plasmas^{5, 14-22}. However, most previous works have mainly focused on the conversion of CO₂ 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 CO₂ into CO and oxygen at low temperature. The synergistic effect resulting from the combination of plasma and photocatalysts (BaTiO₃ and TiO₂) 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 CO₂ 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. CO₂ 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 BaTiO₃ (TCU) and TiO₂ (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 reactions⁶. 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-K α radiation in the 2 θ 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 K α (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), CO₂ conversion (C_{CO₂}) and energy efficiency (E) are defined as follows:

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

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

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

Results and discussion

Plasma-assisted conversion of CO₂ without catalyst

FIG. 2 SHOWS THE EFFECT OF SPECIFIC ENERGY DENSITY (SED) ON THE CONVERSION OF CO₂ AND THE ENERGY EFFICIENCY OF THE PLASMA REACTION IN THE ABSENCE OF A CATALYST. CLEARLY, INCREASING THE SPECIFIC ENERGY DENSITY SIGNIFICANTLY ENHANCES CO₂ CONVERSION DUE TO THE INCREASE IN ENERGY INPUT TO THE DISCHARGE. THE CONVERSION OF CO₂ 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 DISCHARGE²⁵⁻²⁷, 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 CO₂ 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 RESULTS²⁸. 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 CO₂ FEED FLOW RATE OF 60 ML/MIN AND A DISCHARGE LENGTH OF 150 MM.

CO₂ DISSOCIATION BY ELECTRON IMPACT VIBRATIONAL EXCITATION (EQS 4-5) IS BELIEVED TO BE THE MOST EFFECTIVE PATHWAY FOR CO₂ CONVERSION IN COLD PLASMAS, WHICH CAN LEAD TO A HIGH ENERGY EFFICIENCY OF MORE THAN 60%²⁹.

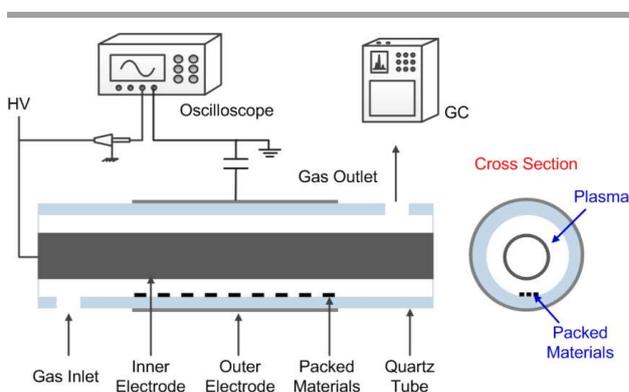
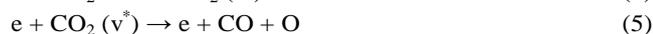


Fig. 1 Schematic diagram of the experimental setup.

WHERE v^* IS THE VIBRATIONAL EXCITED STATE. UP TO 97% OF THE TOTAL PLASMA ENERGY CAN BE TRANSFERRED FROM ELECTRONS TO

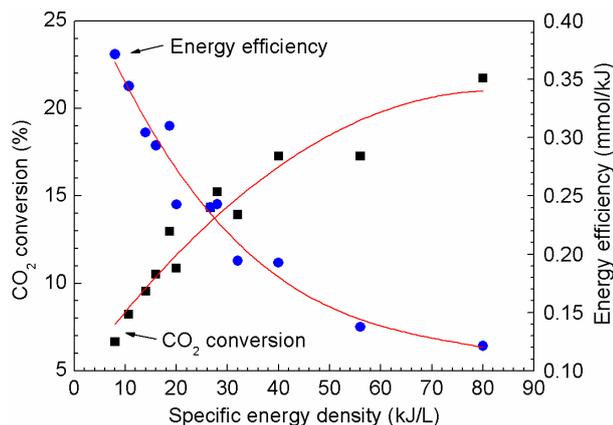


Fig. 2 CO₂ conversion and energy efficiency as a function of specific energy density (SED).

VIBRATIONAL EXCITATION OF CO₂ IF THE PLASMA DISCHARGES HAVE AN ELECTRON TEMPERATURE OF 1-2 eV, OR A REDUCED ELECTRIC FIELD (E/N) OF 20–40 Td²⁹. RECENT PLASMA MODELLING OF CO₂ SPLITTING BY A DBD SHOWED 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 CO₂, RESPECTIVELY³⁰. THEIR RESULTS SHOWED THAT THE MAJORITY (94%) OF CO₂ CONVERSION IS INDUCED BY REACTIONS (E.G. DISSOCIATION) WITH GROUND STATE CO₂ (SHOWN IN EQ. 6) AND ONLY 6% OF CO₂ CONVERSION IS BY REACTIONS WITH VIBRATIONAL EXCITED CO₂ AT A HIGH ELECTRIC FIELD³⁰.



THE ELECTRON IMPACT DISSOCIATION OF CO₂ IN ITS VIBRATIONAL EXCITED STATES (EQ. 5) OR GROUND STATE (EQ. 6) WILL MOST LIKELY RESULT IN CO IN ITS GROUND STATE (¹Σ) AND O ATOMS IN BOTH THE GROUND STATE (³P) AND METASTABLE STATE (¹D). HOWEVER, SINCE CO BANDS WERE OBSERVED IN THE EMISSION SPECTRA OF THE CO₂ DBD, CO COULD ALSO BE FORMED IN EXCITED STATES⁶.

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 LISSAJOUS FIGURE AND BOLSIG⁺ CODE BASED ON ELECTRON ENERGY DISTRIBUTION FUNCTION (EEDF), RESPECTIVELY^{10, 31}. THIS SUGGESTS THAT THE ELECTRON IMPACT VIBRATIONAL EXCITATION OF CO₂ MIGHT PLAY A DOMINANT ROLE IN CO₂ 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 CO₂ MOLECULE (EQ. 8).



OXYGEN MIGHT ALSO BE GENERATED DIRECTLY BY ELECTRON IMPACT DISSOCIATION OF CO₂ IF THE ELECTRON HAS A HIGH ENERGY (> 15 eV).

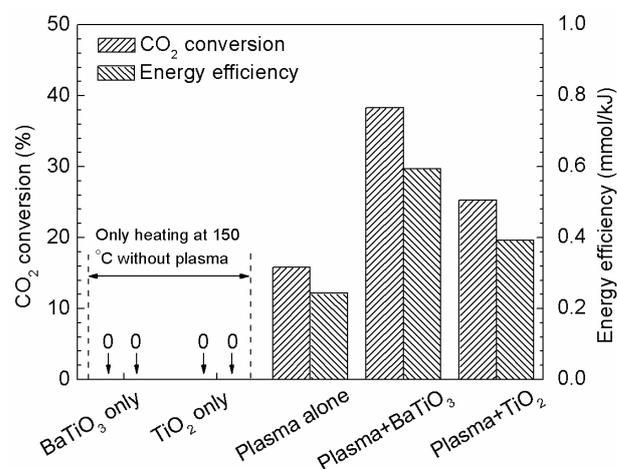


Fig. 3 Demonstration of the synergistic effect of plasma-catalysis for the conversion of CO₂ (SED = 28 kJ/L).



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:



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.



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.

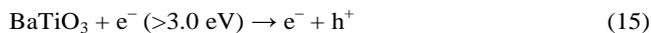
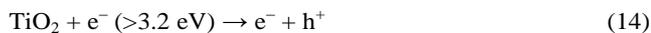
Catalysts can be integrated into a DBD system in different ways. The presence of the catalyst pellets in part of the gas gap still shows predominantly filamentary discharges and surface discharges on the catalyst surface, which induces effective interactions between plasma and catalyst for CO_2 activation. In this work, the dielectric constant of BaTiO_3 and TiO_2 is 10000 and 85, respectively. Previous experimental^{32, 33} and simulation^{34, 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 field²⁶. 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:



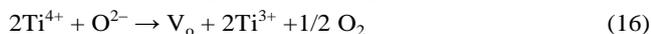
Plasma discharges can generate UV radiation without using any extra UV sources (e.g. UV lamps). This has been confirmed by the dominated N_2 (C-B) bands (between 300 nm and 400 nm) in a CO_2 DBD in our previous work^{6, 39}. However, UV radiation

generated by plasma discharges is not always the controlling factor to activate photocatalysts⁴⁰. 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^{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_o) to enhance the photoexcitation process⁴². In this study, the highly energetic electrons generated by plasma are considered the main driving force to activate the photocatalysts for CO_2 conversion.



Previous investigation has shown that the photocatalytic conversion of CO_2 is a multistep process, which involves the adsorption and subsequent activation of CO_2 molecules on the surface of photocatalysts and the dissociation of the C-O bond. The key step is the activation of CO_2 molecules through the transfer of trapped electrons to adsorbed CO_2 molecules in the V_o ⁴³.

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_2 conversion⁴³. The defect disorders in photocatalysts, such as V_o , play an important role in the CO_2 reduction processes. V_o has been considered as the active site for the adsorption and activation of reactants in a photocatalytic reaction⁴⁴. 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 $BaTiO_3$ sample. Two components (Ti 2p_{3/2} and Ti 2p_{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 $BaTiO_3$; whilst the Ti 2p_{3/2} and Ti 2p_{1/2} peaks of Ti^{3+} are located at around 457.85 eV and 463.67 eV. The presence of Ti^{3+} in the $BaTiO_3$ sample demonstrates the formation of V_o on the catalyst surface through the following reaction^{45, 46}:



where O^{2-} is the lattice oxygen. Clearly, the formation of V_o is followed by the change in the oxidative state of the vicinal Ti from Ti^{4+} to Ti^{3+} to retain the balance of local charge. Similarly, the Ti 2p_{3/2} and Ti 2p_{1/2} peaks of Ti^{3+} can also be detected in the XPS profile of TiO_2 , as shown in Fig. 4(b). We find that there are more Ti^{3+} species in the $BaTiO_3$ (60.86%) sample than in the TiO_2 (49.89%), which suggests more active sites (V_o) were formed in the $BaTiO_3$ catalyst, resulting in the higher CO_2 conversion using the $BaTiO_3$ catalyst.

Moreover, the combination rate of electron-hole pairs can also be significantly reduced in a plasma-photocatalytic system due to

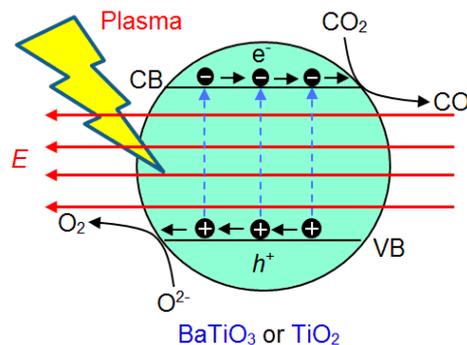
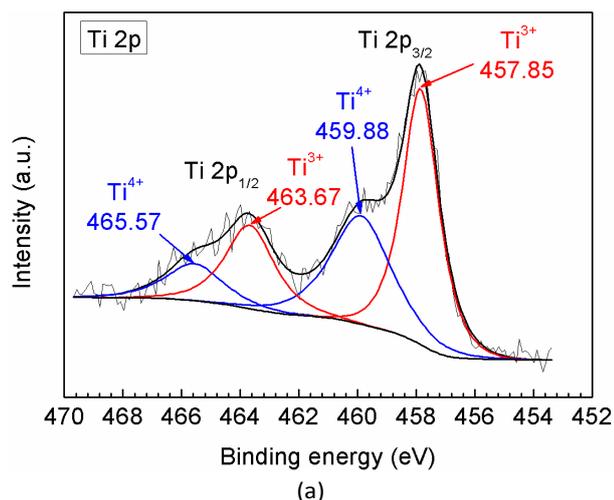


Fig. 5 Schematic of the plasma-catalytic conversion of CO₂ on the photocatalysts.

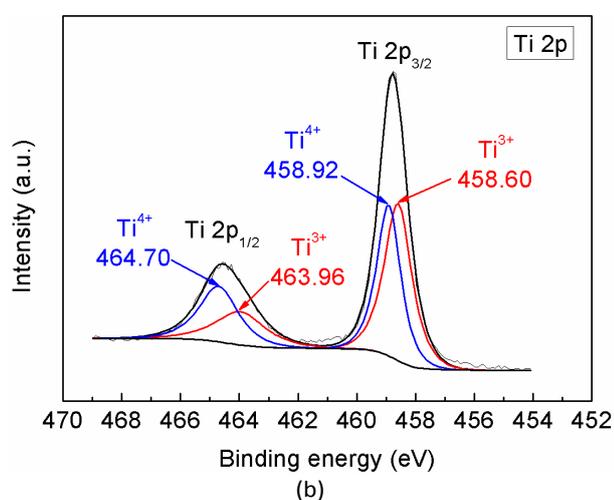
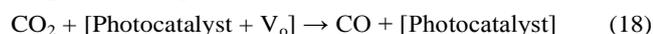


Fig. 4 XPS spectra of Ti 2p peaks for (a) BaTiO₃; (b) TiO₂.

the presence of the electric field and the interactions between the plasma and photocatalyst⁴⁷. In this study, the process of plasma-photocatalytic conversion of CO₂ 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, CO₂ adsorbed in the V_o is reduced to the anion radical CO₂^{•-} by electrons (Eq.17), followed by the decomposition of CO₂^{•-} into CO and the occupation of one oxygen atom in the V_o site. The overall reaction is expressed in Eq.18^{43, 48}, in which [Photocatalyst + V_o] and [Photocatalyst] represent the defective and defect-free photocatalysts, respectively.



In addition, V_o can be regenerated by oxidising the surface O²⁻ anions using holes, followed by releasing O₂, as shown in Eq. 19. To balance the charge, the Ti⁴⁺ in the vicinity of the regenerated V_o can be reduced to Ti³⁺ 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 CO₂, which can be confirmed by our experimental results as the CO₂ 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 CO₂ 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

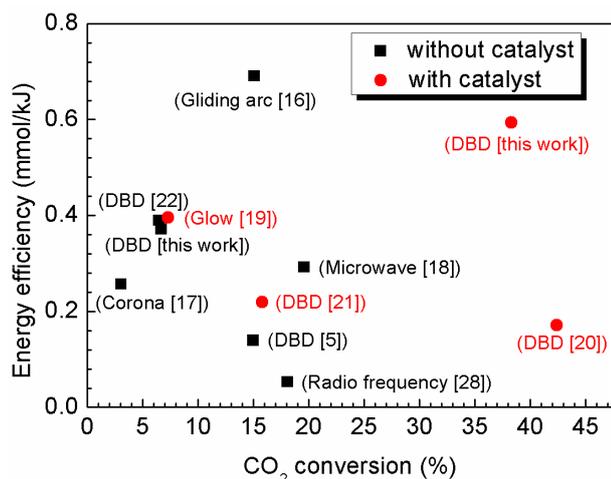


Fig. 6 Comparison of energy efficiency for CO₂ conversion with different plasma processes.

Fig. 6 shows a comparison of the energy efficiency for CO₂ conversion when using different cold plasmas. It is clear that the energy efficiency of the plasma CO₂ 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 CO₂ 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 voltage⁵¹. 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 photo catalysts).

Conclusions

In this study, plasma-photocatalytic conversion of CO₂ into CO and O₂ has been investigated using a DBD reactor combined with BaTiO₃ and TiO₂ catalysts. The combination of plasma with BaTiO₃ and TiO₂ catalysts has shown a synergistic effect, which significantly enhances the conversion of CO₂ 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 CO₂. The overall synergistic effect resulting from the integration of DBD with photocatalysis for CO₂ 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.

Acknowledgements

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