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# Probing the impact of material properties of core-shell SiO<sub>2</sub>@TiO<sub>2</sub> spheres on the plasma-catalytic CO<sub>2</sub> dissociation using a packed bed DBD plasma reactor

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## Abstract

Plasma catalysis, a promising technology for conversion of CO<sub>2</sub> into value-added chemicals near room temperature, is gaining increasing interest. A dielectric barrier discharge (DBD) plasma has attracted attention due to its simple design and operation at near ambient conditions, ease to implement catalysts in the plasma zone and upscaling ability to industrial applications. To improve its main drawbacks, being relatively low conversion and energy efficiency, a packing

material is used in the plasma discharge zone of the reactor, sometimes decorated by a catalytic material. Nevertheless, the extent to which different properties of the packing material influence plasma performance is still largely unexplored and unknown. In this study, the particular effect of synthesis induced differences in the morphology of a TiO<sub>2</sub> shell covering a SiO<sub>2</sub> core packing material on the plasma conversion of CO<sub>2</sub> is studied. TiO<sub>2</sub> has been successfully deposited around 1.6-1.8 mm sized SiO<sub>2</sub> spheres by means of spray coating, starting from aqueous citratoperoxotitanate(IV) precursors. Parameters such as concentration of the Ti(IV) precursor solutions and addition of a binder were found to affect the shells' properties and surface morphology and to have a major impact on the CO<sub>2</sub> conversion in a packed bed DBD plasma reactor. Core-shell SiO<sub>2</sub>@TiO<sub>2</sub> obtained from 0.25M citratoperoxotitanate(IV) precursors with the addition of a LUDOX binder showed the highest CO<sub>2</sub> conversion 37.7% (at a space time of 70 s corresponding to an energy efficiency of 2%) and the highest energy efficiency of 4.8% (at a space time of 2.5 s corresponding to a conversion of 3%).

## **Keywords**

Plasma catalysis; CO<sub>2</sub> splitting; DBD plasma; core-shell SiO<sub>2</sub>@TiO<sub>2</sub> spheres; solution deposition

## **1. INTRODUCTION**

Carbon dioxide (CO<sub>2</sub>) is considered as one of the main contributors to global warming and concomitant climate change. Continuous consumption of fossil fuels for energy, transportation and some specific industrial processes is responsible for the gradual increase in the atmosphere's CO<sub>2</sub> concentration [1]. The unavoidable excess CO<sub>2</sub> in the atmosphere, which cannot be prevented, can be mitigated by its capture and storage [2]. Even though CO<sub>2</sub> capture and storage can play a role in lowering the amount of CO<sub>2</sub> in the atmosphere, the technology to achieve this is still restricted by high investment costs and uncertainty of potential long-term storage [3, 4]. Utilization of CO<sub>2</sub> by transforming it into value-added chemicals has gained significant attention in view of a future sustainable carbon-neutral economy in chemical and energy industries [4-6]. Several methods have been put forward to convert CO<sub>2</sub> into value-added chemicals, such as dry reforming of CH<sub>4</sub> [7-9], CO<sub>2</sub> dissociation [10, 11], or CO<sub>2</sub> hydrogenation to methanol [12], hydrocarbons [13, 14] or formaldehyde [15]. Direct splitting of pure CO<sub>2</sub> into CO and O<sub>2</sub> is an industrially important process, whereby CO is used as feedstock for other value-added products [16, 17]. The direct splitting of CO<sub>2</sub> into CO and O<sub>2</sub> is however a highly

endothermic reaction ( $\Delta H_{298K} = 279.8$  kJ/mol) due to the large amount of energy required to break the C=O bonds [18]. In conventional thermal catalysis, dissociation of CO<sub>2</sub> is achieved at 2000 K with low conversion rate (<1%). The highest CO<sub>2</sub> conversion (60%) was attained at extremely high temperature (3000-3500 K) [19, 20]. Non-thermal plasma (NTP) catalysis is an attractive alternative for conventional thermal catalysis, which activates CO<sub>2</sub> at near ambient conditions [21]. In a plasma, reactive species like electrons, ions, radicals and excited species are obtained by applying a high voltage to a gas. This provides energy, mainly to the light electrons, in the range of 1-10 eV (~ 10,000-100,000 K) [22], which is enough to break the C=O bond at ambient conditions (bond dissociation energy for CO<sub>2</sub> is 5.5 eV). The most commonly used plasma types for CO<sub>2</sub> conversion by direct splitting are microwave (MW) [23-25], gliding arc (GA) [26-28] and dielectric barrier discharge (DBD) plasma's [10, 11, 29-32], each with its own benefits and drawbacks. DBD reactors are well-known for their simple, robust design and relatively easy scalability towards industrial applications [33]. Their major advantage is their operation near room temperature and pressure and the possibility to implement materials in the plasma zone that can provide physical and possibly catalytic enhancements of the plasma processes.

Although plasma alone can convert CO<sub>2</sub> into CO, the main drawback of a DBD plasma is the low conversion and energy efficiency. It can be improved by the introduction of (catalyst) packing materials in the DBD reactor [34]. Recent studies focus on both reactor parameters (such as plasma power or discharge gap) and characteristics of the packing material (such as bead size, composition or presence of a catalyst) on CO<sub>2</sub> dissociation in DBD plasma aiming for a higher conversion and energy efficiency. Different packing materials have been investigated in CO<sub>2</sub> dissociation, such as SiO<sub>2</sub> [10, 11], Al<sub>2</sub>O<sub>3</sub> [35], ZrO<sub>2</sub> [36], BaTiO<sub>3</sub> [37], quartz wool [34], ceramic foams [38], etc. As demonstrated in the above papers, the introduction of packing materials in the DBD reactor (often, but not always) enhances the CO<sub>2</sub> dissociation. Moreover, a combined effect of reactor parameters and packing materials' properties has been reported as well [31]. In these, it is postulated that synergistic effects between plasma and catalysts/packing material can enhance the conversion. However, this interaction between the plasma and material surface is still poorly understood [39].

The effect of the packing material properties, such as its crystalline phase, surface morphology or a composite composition, on CO<sub>2</sub> conversion did not gain significant attention. Introduction of a combination of oxides in the form of core-shells or the use of mixed metal oxides is nevertheless expected to influence the plasma properties at the packing material surface and

hence the conversion. In order to develop unambiguous insights into the effect of these factors, it is important to study the plasma process using packing materials with a systematically controlled structure and composition. Core-shell materials have been studied extensively in many applications because of the different chemical composition/combined effect on the surface and bulk [40]. However, there are only a few reports on core-shell structured materials in plasma catalysis [41-43]. To our knowledge, not many research has been reported on the influence of material properties on millimetre-sized core-shell spheres, as we investigated here. In addition, the properties of TiO<sub>2</sub> in plasma catalysis in the form of core-shell structures have not yet been explored. Here, a core-shell SiO<sub>2</sub>@TiO<sub>2</sub> packing material has been introduced in a plasma-catalytic CO<sub>2</sub> dissociation in a DBD plasma reactor.

Titania (TiO<sub>2</sub>) is a semiconductor material, widely investigated in many fields. It has a dielectric constant of 85-100, which can be the driving force to generate high energy electrons and localized dielectric discharges in plasma catalysis. In addition, Mei et al. also demonstrated the plasma-photocatalytic behaviour in TiO<sub>2</sub> and BaTiO<sub>3</sub> packing in CO<sub>2</sub> dissociation and reported a factor 2.5 enhancement of the conversion and energy efficiency in comparison to the reaction without the packing material [37]. It was suggested that the combined effect of semiconductor, photocatalytic and dielectric properties of TiO<sub>2</sub> might have an advantage in plasma-catalytic CO<sub>2</sub> dissociation [39]. Based on its semiconducting nature, its known oxygen vacancies and Ti<sup>3+</sup>/Ti<sup>4+</sup> transitions and surface charging, titania materials may have an interaction with the plasma species (radicals, ions, electrons or photons) that might influence conversion [39, 44]. Silica (SiO<sub>2</sub>) is one of the most widely applied packing materials in packed bed DBD plasma reactors. Moreover, a combination of SiO<sub>2</sub> with titania (TiO<sub>2</sub>) to form a composite material has been suitable for many catalytic processes, resulting in the enhancement of catalytic, structural and chemical properties [45]. Hence, TiO<sub>2</sub> is chosen as a shell layer for mm range core SiO<sub>2</sub> spheres as it might induce both physical (e.g. discharge, electric field enhancements) and chemical (surface) effects that influence plasma based CO<sub>2</sub> conversion.

TiO<sub>2</sub> has three main polymorphs namely anatase, rutile and brookite [46]. Of the three, anatase is one of the most widely studied crystal structure in many applications, like photocatalysis [47], heterogeneous thermal catalysis [48], photoelectrocatalysis [49], etc. Because of polymorphism, it is important to choose a suitable synthesis method for the coating process to achieve a core-shell SiO<sub>2</sub>@TiO<sub>2</sub> with a controlled titania crystal phase. Requirements for the synthesis of the titania shell are that the precursor solution has good stability, the layer adheres well to the beads and the crystal structure is controlled and uniform. Several methods, such as sol-gel [50, 51],

hydrothermal [52], solvothermal [53] routes, etc., allow to successfully synthesize core-shell  $\text{SiO}_2@\text{TiO}_2$  nanoparticles in a controlled way. However, in the DBD plasma reactor, the packing materials have dimensions in the mm range. As such large core spheres have a much stronger tendency to sediment, compared to nanosized core particles, the coating with a shell requires an adapted deposition approach, which has been developed in this work. When coating micrometer and millimeter sized materials, binders are often used to improve the homogeneous deposition on the packing materials. The contact surface between shell and core packing materials increases by the addition of binder, which improves adhesion. Mainly colloidal silica and alumina binders have been investigated depending on the application [54, 55]. Alumina has higher thermal stability than silica [55]. However, in this study, we opted for a binder with the same chemical composition as the support (core) because a different chemical composition could influence the packing material's physical and chemical properties towards the plasma, causing a strong influence on the catalytic performance.

Hence, a chemical solution based procedure was investigated to coat the mm range  $\text{SiO}_2$  spheres with a  $\text{TiO}_2$  layer by means of spray coating using stable water-based precursor solutions of citratoperoxotitanate(IV) complexes with and without the addition of a silica-based binder. We particularly focus on understanding the particular effect of the synthesis induced differences in the morphology of a  $\text{TiO}_2$  shell, covering a  $\text{SiO}_2$  core packing material, on the changes in plasma-catalytic  $\text{CO}_2$  dissociation induced by the modified material properties such as surface morphology and loading of  $\text{TiO}_2$ .

## **2. Experimental Section**

### **2.1. Chemicals required**

The following chemicals were used for the preparation of the Ti(IV) precursor solution: titanium isopropoxide ( $\text{Ti}(\text{OC}_3\text{H}_7)_4$ , 98%, Acros), citric acid ( $\text{C}_6\text{H}_8\text{O}_7$ , 99.5%, Sigma-Aldrich), hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 35 wt% in  $\text{H}_2\text{O}$ , Merck), ammonia ( $\text{NH}_3$ , 32% in  $\text{H}_2\text{O}$ , extra pure, Merck), non-porous  $\text{SiO}_2$  spheres (1.6-1.8 mm, SiLibeads-type S, Sigmund Lindner) and LUDOX HS-40 colloidal silica as a binder (40 wt% suspension in  $\text{H}_2\text{O}$ , Merck).

### **2.2. Synthesis of aqueous citratoperoxotitanate(IV) precursor solution**

An aqueous citratoperoxotitanate(IV) precursor solution was prepared following the reported route by Hardy et al. [56]. An appropriate volume of Ti(IV) isopropoxide (0.10 to 2.50 M) was added into an excess of  $\text{H}_2\text{O}$ . The white precipitate, formed as a result of hydrolysis and condensation, was collected via filtration and washed with water to remove byproducts. The

obtained wet white precipitate was then mixed with a solution of 3M citric acid (molar ratio of 1:1 against  $Ti^{4+}$ ) and 35 wt% hydrogen peroxide (molar ratio of 1.5:1 against  $Ti^{4+}$ ). This mixture was heated at 60°C under constant stirring. After the precipitate dissolved, the solution's colour turned into dark red. Next, the pH of the dark red solution was adjusted to 7 by the dropwise addition of 32% ammonia. In this step, the dark red solution turned yellow-orange. The obtained solution was heated at 80°C for 30 minutes. By the addition of water, different concentrations of citratoperoxotitanate(IV) precursor solutions ranging from 0.10 to 2.50 M were prepared.

To study the effect of adding a binder (LUDOX), three different concentrations of citratoperoxotitanate(IV) precursor (0.10, 0.25 and 0.50 M) solutions were prepared with and without LUDOX, respectively. In a 100 ml citratoperoxotitanate(IV) precursor solution, 0.1 wt% of LUDOX (against  $Ti^{4+}$ ) was added and stirred for 1 hour.

**Table 1:** Experimental parameters of the precursor solutions used to prepare the core-shell spheres. The sample code  $SiO_2@TiO_2 - xM$  indicates that a precursor solution of x M Ti(IV) was used to spray coat around  $SiO_2$  spheres. '+ LUDOX' is added to the sample code if a binder was mixed with the precursor solution prior to spray coating.

Sample code	Concentration of citratoperoxotitanate(IV) precursor solution (M)	LUDOX <sup>a</sup> (wt% vs $Ti^{4+}$ )
$SiO_2$	-	-
$SiO_2@TiO_2 - 0.10M$	0.10	-
$SiO_2@TiO_2 - 0.25M$	0.25	-
$SiO_2@TiO_2 - 0.50M$	0.50	-
$SiO_2@TiO_2 - 0.10M+LUDOX$	0.10	0.1
$SiO_2@TiO_2 - 0.25M+LUDOX$	0.25	0.1
$SiO_2@TiO_2 - 0.50M+LUDOX$	0.50	0.1
$SiO_2@SiO_2 - 1.00M+LUDOX$	1.00	0.1
$SiO_2@TiO_2 - 1.50M+LUDOX$	1.50	0.1
$SiO_2@TiO_2 - 2.00M+LUDOX$	2.00	0.1
$SiO_2@TiO_2 - 2.50M+LUDOX$	2.50	0.1

### 2.3. Spray Coating

The as-prepared citratoperoxotitanate(IV) precursor solutions with and without binder was spray coated onto SiO<sub>2</sub> spheres by means of a homebuilt drum spray coater [41]. The coated spheres dry during the spray coating process by a hot airflow. The coated SiO<sub>2</sub> core-shell spheres were then collected from the drum spray coater and calcined in a furnace at 650°C for 4 hours in an ambient atmosphere, reached with a heating rate of 2°C/min.

All prepared core-shell SiO<sub>2</sub>@TiO<sub>2</sub> spheres were labelled as SiO<sub>2</sub>@TiO<sub>2</sub> – xM (without LUDOX) and SiO<sub>2</sub>@TiO<sub>2</sub> – xM+LUDOX (with LUDOX), where x is the concentration of the citratoperoxotitanate(IV) precursor solution (Table 1).

### 2.4. Plasma-Catalytic Experimental Setup

The experimental setup of the cylindrical packed-bed DBD reactor applied for plasma catalysis of CO<sub>2</sub> dissociation was discussed by Uytdenhouwen et al. [11]. A stainless steel rod with an outer diameter of 8 mm was used as the inner electrode. An alumina dielectric barrier was placed around the inner electrode. Its inner diameter was 17 mm, resulting in a discharge gap of 4.5 mm (between the inner electrode and the barrier). The outer diameter of the barrier was 21.8 mm, corresponding to a barrier thickness of 2.4 mm. A stainless-steel mesh with a length of 100 mm was wrapped around the dielectric tube to form the outer electrode. The inner electrode was grounded, while the outer electrode was powered by a high voltage, supplied by a generator (AFG 2021, Tektronix) and transformer (TREK, Model 20/20C-HS, x2000 voltage amplification). The applied voltage was measured with a high voltage probe (Tektronix P6015A), while a Rogowski coil (Pearson 4100) was used to measure the total current. Moreover, the voltage was measured on an external capacitor (10nF) to obtain the generated charges (Q) in the plasma. Finally, all electrical signals were recorded by an oscilloscope (Picotech, PicoScope 6402 D).

### 2.5. Space time measurements and extraction of kinetics data

The synthesized core-shell SiO<sub>2</sub>@TiO<sub>2</sub> spheres (~ 23 ml) were packed in the entire discharge area with quartz wool at both ends of the reactor to hold the bed in place. Pure CO<sub>2</sub> gas was fed and controlled by a thermal mass flow controller. Plasma-catalytic CO<sub>2</sub> dissociation measurements of both packed and unpacked reactors were tested at a constant feed flow rate of 39 ml/min. While adding packing materials, the reactor volume decreased by 48.27% [31], so the feed flow was adjusted to 75 ml/min in the unpacked reactor to create a similar space time as the packed reactor with a feed flow rate of 39 ml/min (space time of 14.07 s). To study the



impact of the packing materials, the other experimental parameters, such as plasma power, frequency and discharge gap, were fixed at a constant value of 30 W, 3 kHz and 4.5 mm, respectively.

Moreover, the effect of the flow rate (space time) on the performance of the spherical core-shell packed reactor was evaluated by applying different feed flow rates, ranging from 8 to 219 ml/min (space time ranging from 2.5 to 70 s). More specifically, by tracking the reactor performance over a wide range of space times, key valuable kinetics data can be determined. Uytdenhouwen et al. developed an apparent first order reversible reaction to fit the experimental data and retrieve the equilibrium conversion and an overall reaction rate coefficient, as well as the individual CO<sub>2</sub> loss and formation rate coefficients, to quantify the reactor performance more fundamentally [31, 41, 57]. The equation (with derivation found in [57]) is defined as:

$$x_A(t) = x_{A,e} - (x_{A,e} - x_{A,i}) e^{-kt}, \quad (1)$$

where  $x_{A,e}$  and  $x_{A,i}$  are the equilibrium and initial mole fraction of A (with  $x_{A,i} = 1$  for CO<sub>2</sub> dissociation),  $t$  is the space time and

$$k = f k_{\text{form}} + k_{\text{loss}} \quad (2)$$

$$x_{(A,e)} = \frac{f k_{\text{form}}}{f k_{\text{form}} + k_{\text{loss}}}. \quad (3)$$

$k$  is the overall apparent rate coefficient with  $k_{\text{loss}}$  and  $f k_{\text{form}}$  the apparent CO<sub>2</sub> loss and formation rate coefficients, respectively. The  $f$  factor is a constant that depends on the elemental composition of the system.

The equilibrium mole fraction  $x_{A,e}$  can be rewritten in terms of the total equilibrium conversion  $X_e$  as:

$$X_e = \frac{k_{\text{loss}}}{f k_{\text{form}} + k_{\text{loss}}}. \quad (4)$$

The experimental data is fitted to equation (1) with MATLAB to retrieve  $k$  and  $x_e$ , and subsequently calculate the remaining values via equations (2) to (4).

## 2.6. Conversion and energy efficiency

The gas at the outlet of the reactor was analyzed by gas chromatography (GC) (Compact GC, Interscience). The GC is equipped with a thermal conductivity detector (TCD) and a flame

ionization detector, and 4 columns: a Molsieve 5A, 2 RT-Q bonds and an RTX-f column. The conversion of CO<sub>2</sub>, X<sub>CO<sub>2</sub></sub>, from the GC data was determined by the following equation:

$$X_{CO_2} = \frac{CO_{2,in} - CO_{2,out}}{CO_{2,in}} \times 100\% \quad (5)$$

As one mole of CO<sub>2</sub> splits into 1 mole of CO and 0.5 mole of O<sub>2</sub>, this gives a gas expansion factor of 1.5 for 100% conversion. As in the GC, the sample loop is depressurized to atmospheric pressure while injecting the reaction sample, some of the molecules are not detected when expansion of the gas has taken place. This causes an apparent lower peak area and CO<sub>2</sub> concentration and leads to an overestimation of CO<sub>2</sub> conversion. Therefore, the overestimated conversion has to be corrected, based on the actual gas conversion and expansion. The actual CO<sub>2</sub> conversion can be calculated by the following equation, defined by Pinhão et al. [58] and Snoeckx et al. [59].

$$X_{GC} = 1 - \left( \frac{1 - X_{CO_2}}{1 + \frac{X_{CO_2}}{2}} \right) \leftrightarrow X_{CO_2} = \frac{2X_{GC}}{3 - X_{GC}} \quad (6)$$

The energy efficiency of the conversion can be calculated via the following formula:

$$\eta (\%) = \frac{\Delta H_r \left( \frac{kJ}{mol} \right) * X_{CO_2} (\%)}{SEI \left( \frac{kJ}{L} \right) * 24.5 \left( \frac{L}{mol} \right)} \quad (7)$$

Where ΔH<sub>r</sub> is the reaction enthalpy of CO<sub>2</sub> dissociation (283 kJ/mol at 298.15 K), X<sub>CO<sub>2</sub></sub> is the actual CO<sub>2</sub> conversion and a constant plasma power of 30 W is used to calculate the specific energy input (SEI) from the formula as follows

$$SEI \left( \frac{kJ}{L} \right) = \frac{Plasma Power (kW)}{Flow Rate \left( \frac{L}{min} \right)} * 60 \left( \frac{s}{min} \right) \quad (8)$$

All the experiments were carried out with a freshly packed, cooled-down reactor and operated for a minimum amount of time of 40 min, to reach a thermal steady-state behaviour. The input voltage amplitude was continuously adjusted to the desired power of 30 W during the stabilization. Each experiment was tested in threefold for statistical review and for each experiment 4 GC measurements are taken, resulting in twelve data points per condition. The error bars were defined as:

$$error = \pm S_n \frac{T(p, n_s)}{\sqrt{n_s}} \quad (9)$$

With  $S_n$  the sample standard deviation of the measurements,  $n_s$  the sample size (12), and  $T$  the two-tailed inverse of the Student's t-distribution for sample size  $n_s$  and probability  $p$  set at 95%.

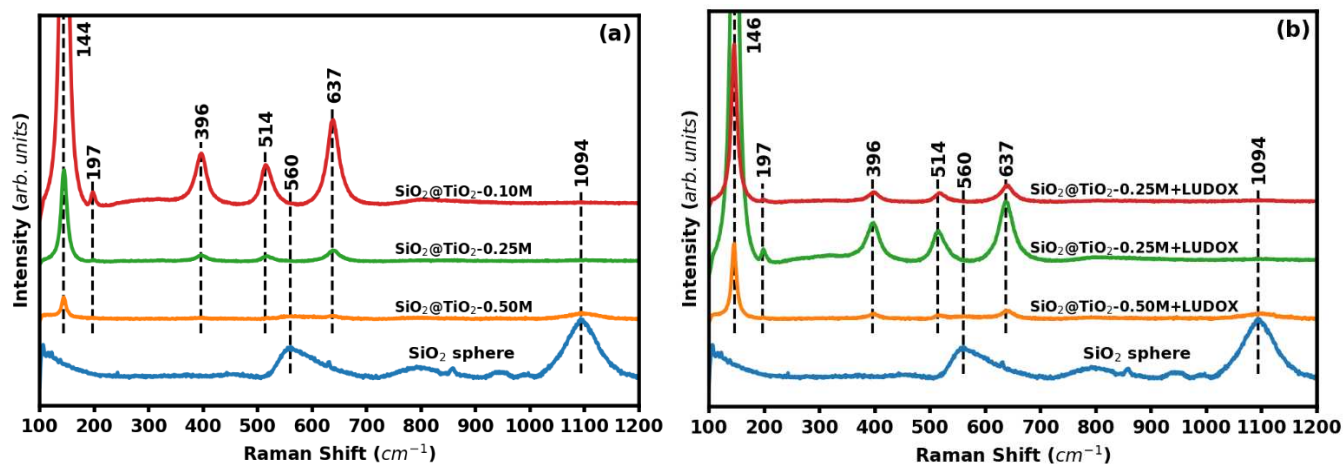
## 2.7. Chemical and physical characterization

Raman spectroscopy was performed with a Horiba Jobin Yvon T64000 triple Raman spectrometer, equipped with a BXFM Olympus microscope (10x magnification objective), a Horiba Jobin Yvon Symphony CCD detector and a 488 nm Lexel SHG laser operated at approximately 20 mW and with a spot size diameter of 2.381  $\mu\text{m}$ . The confocal hole diameter was minimized to improve the spatial resolution. Raman spectroscopy recorded in all core-shell packing materials were measured at multiple spots of several spheres. The surface morphology of the (coated) packing spheres was characterized by using scanning electron microscopy (FEI Quanta 200FEG-SEM and Hitachi TM3000). SEM images were taken at multiple spots of several spheres.

## 3. Result and discussion

### 3.1. Titania crystal structure

The three main crystal structures of titania; namely anatase, rutile and brookite, can be identified by vibrational modes in Raman spectroscopy. Given the shape of the samples, it appeared difficult to collect the scattering from similar confocal volumes, and hence comparing intensities among the samples is not straightforward. All observed Raman modes (**Fig. 1(a)**) in  $\text{SiO}_2@ \text{TiO}_2$  – 0.10 M, 0.25 M and 0.50 M packing materials were in good agreement with the reported modes for anatase  $\text{TiO}_2$ . Anatase  $\text{TiO}_2$  has six different Raman modes at 144 ( $E_g$ ), 197 ( $E_g$ ), 399 ( $B_{1g}$ ), 516 (doublets of  $A_{1g}$  and  $B_{1g}$ ) and 639  $\text{cm}^{-1}$  ( $E_g$ ), respectively [60]. The strongest  $E_g$  mode at 144  $\text{cm}^{-1}$  assigned to external vibration of the anatase structure, is well resolved in all core-shell packing materials. This confirms the presence of  $\text{TiO}_2$  around the  $\text{SiO}_2$  spheres. It has been observed in SEM (§3.2) that the dense layer, formed at high concentration (0.5M) reveals poor adhesion with the core layer. It was observed that part of the  $\text{TiO}_2$  layer detaches from the  $\text{SiO}_2$  spheres, which could be due to stress occurring during heat treatment. The appearance of the  $\text{SiO}_2$  Raman band at 1094  $\text{cm}^{-1}$  (**Fig. S1**) in the  $\text{SiO}_2@ \text{TiO}_2$  – 0.50M packing material could therefore be an indication that the  $\text{SiO}_2$  surface becomes more exposed due to detachment of the  $\text{TiO}_2$  layer, which is further confirmed by SEM. The absence of a  $\text{SiO}_2$  Raman band in the other two packing materials ( $\text{SiO}_2@ \text{TiO}_2$  – 0.10M and 0.25M) might point to a more continuous  $\text{TiO}_2$  coverage of the  $\text{SiO}_2$  surface.



**Figure 1.** Raman spectra of core-shell spheres prepared with different concentrations of the Ti(IV) precursor solution (a) without a binder and (b) with a binder (LUDOX).

To study the role of the binder, Raman spectra for the packing materials were investigated, whereby LUDOX was added to the Ti(IV) precursor, which are shown in **Fig. 1(b)**. For all the coated packing materials with LUDOX in the formulation, also the presence of anatase TiO<sub>2</sub> structure is demonstrated. There is no evidence of a phase transition of anatase to rutile for any of the coated spheres, even after heat treatment at 650 °C. Hence, we conclude that all the core-shell packing materials have a pure anatase TiO<sub>2</sub> crystal structure within the detection limit of the Raman spectrometer.

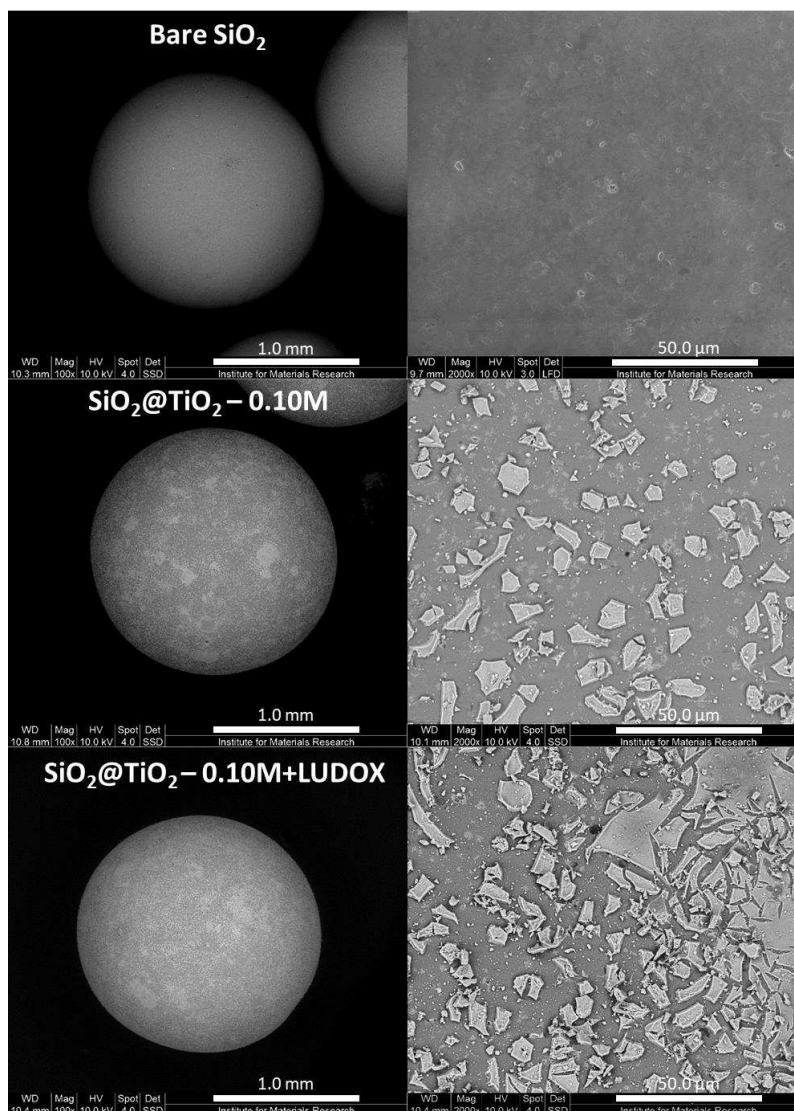
A SiO<sub>2</sub> Raman mode (magnification in **Fig. S1**) can be observed in the core-shell SiO<sub>2</sub>@TiO<sub>2</sub> – 0.50M+LUDOX, which could originate from a higher local presence of silica in the sample resulting from the LUDOX or from SiO<sub>2</sub> constituting the core.

Also after plasma catalysis, the core-shell packing materials were characterized by Raman spectroscopy to inspect if the plasma reaction induces changes in the TiO<sub>2</sub> structure. The results (**Fig. S2**) confirm that the presence of anatase TiO<sub>2</sub> phase is retained even after plasma catalysis. In addition, surface defects such as oxygen vacancies or Ti vacancies can be investigated by Raman spectroscopy. The inset graph in **Fig. S2**. shows no shift or broadening of E<sub>g</sub> mode (146 cm<sup>-1</sup>) was observed, it confirms that there are no surface defects in the spent core-shell packing materials.

### 3.2. Surface Morphology

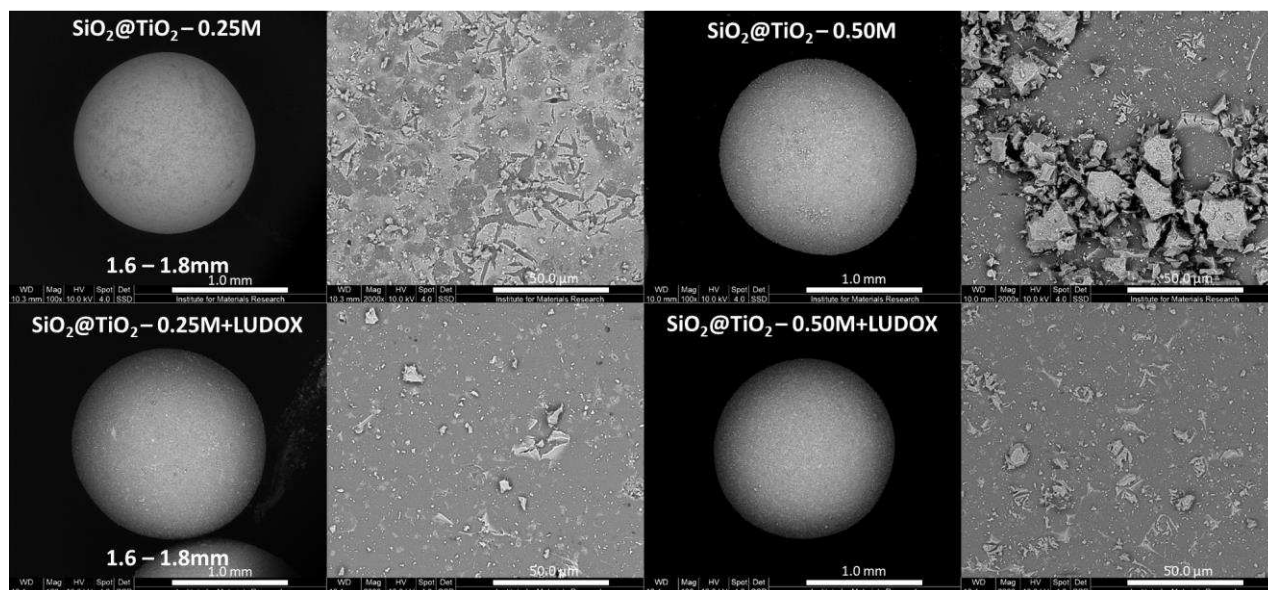
Surface morphology changes play an important role in catalysis, which can have either a positive or negative effect on the activity. More specifically, in case of plasma catalysis, cracks, edges,

and surface roughness could influence the plasma by changes in discharge behavior, local electric field enhancements, etc [39, 61]. To assess the effect of the concentration of the Ti(IV) precursor and the presence or absence of LUDOX in the coating formulation on the surface morphology of the TiO<sub>2</sub>-coated silica spheres, packing materials coated with different concentrations of the citratoperoxotitanate(IV) precursor with and without LUDOX were characterized by scanning electron microscopy (SEM). **Fig. 2** shows the SEM images of bare SiO<sub>2</sub> spheres and SiO<sub>2</sub>@TiO<sub>2</sub> – 0.10M spheres with and without LUDOX. A clear difference can be observed between uncoated and coated packing materials. The bare SiO<sub>2</sub> spheres have a smooth surface with some defects, whereas SiO<sub>2</sub>@TiO<sub>2</sub> – 0.10M spheres with and without LUDOX show the deposition of a non-uniform coating consisting of TiO<sub>2</sub> islands. The TiO<sub>2</sub> structures have a higher backscatter yield compared to the SiO<sub>2</sub> surface and thus are brighter in the backscattered-electron (BSE) imaging mode. The non-uniformity might be due to an insufficient amount of TiO<sub>2</sub> to cover the SiO<sub>2</sub> surface, and/or by removal of organic compounds and crystallization during the heat treatment. However, it can be observed that the cracks formed on the coated SiO<sub>2</sub> surface are somewhat less in the samples with LUDOX compared to those without LUDOX. This illustrates that the addition of LUDOX increases the TiO<sub>2</sub> coverage of the SiO<sub>2</sub> spheres, even though the amount is not sufficient to form a continuous layer.



**Figure 2.** SEM images of bare SiO<sub>2</sub>, core-shell SiO<sub>2</sub>@TiO<sub>2</sub> – 0.10M spheres with and without LUDOX calcined at 650°C.

The coverage of the TiO<sub>2</sub> layer was observed to improve when using higher concentrations of the titania precursor in SiO<sub>2</sub>@TiO<sub>2</sub> – 0.25M spheres (without LUDOX). However, still cracks formed on the surface (**Fig. 3**). SEM images of SiO<sub>2</sub>@TiO<sub>2</sub> – 0.25M packing materials (**Fig. S3**) confirm the formation of cracks even before calcination. Also, the formation of larger cracks due to evolution of gases during calcination can be observed. Nevertheless, further increase in Ti(IV) concentration to 0.50M in the core-shell particle without LUDOX does not provide better coating uniformity, as large flakes of TiO<sub>2</sub> are being formed on the surface (**Fig. 3**). After the calcination step of SiO<sub>2</sub>@TiO<sub>2</sub> – 0.50M, TiO<sub>2</sub> powder was found to be deposited at the bottom of the sample container, indicating that part of the TiO<sub>2</sub> layer detaches and releases from the SiO<sub>2</sub> spherical particles at higher TiO<sub>2</sub> loading.



**Figure 3.** Surface morphology of core-shell  $\text{SiO}_2@\text{TiO}_2 - 0.25\text{M}$  and  $0.50\text{M}$  spheres with and without LUDOX calcined at  $650^\circ\text{C}$ .

The surface coverage improved in all core-shell  $\text{SiO}_2@\text{TiO}_2$  spheres with LUDOX. In the  $\text{SiO}_2@\text{TiO}_2 - 0.25\text{M}+\text{LUDOX}$  and  $0.5\text{M}+\text{LUDOX}$  spheres, the packing materials' surface appears more uniform with fewer cracks. Hence, the addition of LUDOX as a binder seems to improve the adhesion between core and shell layer [55]. SEM images (**Fig. 3**) of coated spheres with LUDOX confirm the improved adhesion between  $\text{SiO}_2$  and  $\text{TiO}_2$ . However, the homogeneity of the coated layers varies on different  $\text{SiO}_2$  spheres. Based on the results, it is clear that both the concentration of the titania precursor as well as the use of a binder material are important to obtain well controlled, crack free coated layers.

Surface morphology of core-shell packing materials has been evaluated after plasma catalysis experiments as well. The SEM images indicated that the surface morphology of the packing materials with LUDOX remained more or less the same as the original packing materials (**Fig. S4**), which suggests a sufficiently strong interaction between the  $\text{SiO}_2$  and  $\text{TiO}_2$  layer even after multipoint-space time measurements.

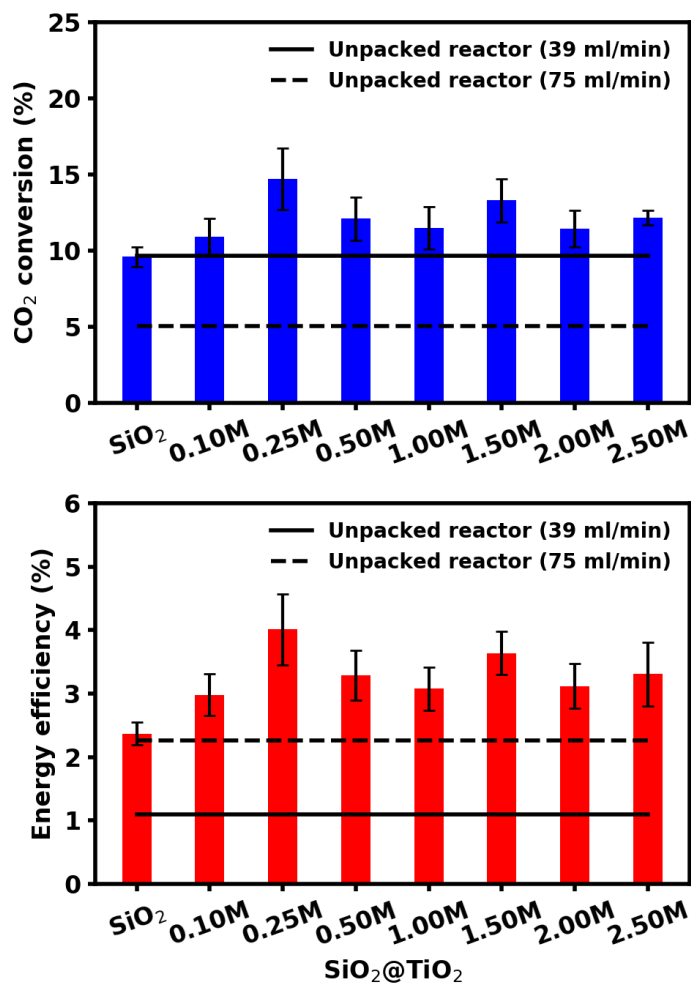
## 4. Plasma-catalytic measurement

### 4.1. Influence of $\text{TiO}_2$ loading

To study the influence of the  $\text{TiO}_2$  loading on the plasma-assisted  $\text{CO}_2$  conversion, the reaction was carried out by using different core-shell packing materials produced with concentrations of citratoperoxotitanate(IV) precursor solutions ranging from 0.10 M to 2.50 M containing LUDOX (**Fig. 4**). All experiments with different core-shell packing materials showed the same or a higher

CO<sub>2</sub> conversion and energy efficiency compared to the unpacked reactor or bare SiO<sub>2</sub> spheres as reference systems, irrespective of the flow rate. Although at a flow rate of 39 ml/min (similar to the packed reactor), the positive effect of the packing on the conversion is present, in most cases it is relatively small (in the range of 4-5% more conversion) taken into account the error bars (1-2%). Nevertheless, it demonstrates that the introduction of a dielectric material (TiO<sub>2</sub>) as a shell layer on SiO<sub>2</sub> spheres is able to enhance the conversion, as also indicated in literature [37]. When the concentration of the Ti(IV) solution increases from 0.10 M to 0.25 M, the CO<sub>2</sub> conversion increases by 4%. However, a further increase in the concentration to 0.50 M leads to a decrease in conversion by 3%. The conversion and energy efficiency remain more or less constant when increasing the concentration further from 0.50 M to 2.50 M. Based on the data of conversion and the morphological characteristics described before, this confirms that core-shell spheres prepared with a low concentration of Ti(IV) precursor solutions (as is the case for 0.25 M and 0.50 M) might be more beneficial. A further increase in the concentration results in TiO<sub>2</sub> layers that peeled off from the SiO<sub>2</sub> spheres, which causes more exposed SiO<sub>2</sub> surface and surface roughness with edges and SiO<sub>2</sub>/TiO<sub>2</sub> contacts and is likely responsible for the lower conversion. When compared with the unpacked reactor at the same space time, the conversion is significantly higher for core-shell packing materials with lower concentration of Ti(IV) precursor solutions. Also, the energy efficiency of the core-shell packing materials are much higher than the unpacked reactor. Here the increase is much larger when compared at same flow rate, but even at same space time, the energy efficiency is higher (in spite of the higher SEI). Hence, SiO<sub>2</sub>@TiO<sub>2</sub> – 0.10M, 0.25M and 0.50M spheres (with LUDOX) were chosen as optimized packing materials for further measurements.



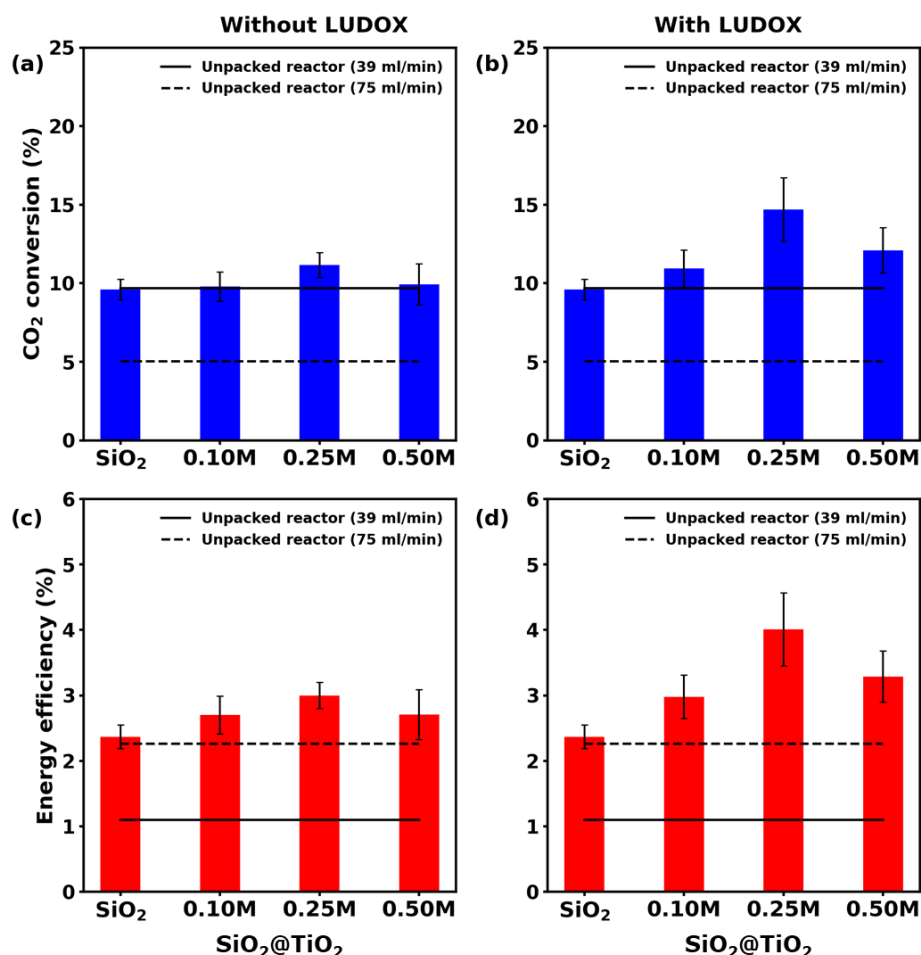


**Figure 4.** Plasma-catalytic CO<sub>2</sub> conversion and corresponding energy efficiency, in function of the different concentrations of Ti(IV) precursor solutions with LUDOX coated on SiO<sub>2</sub> spheres, compared to the unpacked reactor at the same flow rate (39 ml/min) and at the same space time (14.07 s; flow rate of 75 ml/min).

#### 4.2. Impact of LUDOX as a binder

As observed from Raman spectra and SEM images, a binder (LUDOX) was used to improve the uniformity of the TiO<sub>2</sub> shell layer. The effect of the binder on the conversion and energy efficiency was studied by comparing the CO<sub>2</sub> conversion using core-shell spheres with and without LUDOX in the DBD reactor. All the measurements were performed at 14.07 s space time, where the conversion results show a significant difference in the packing material with and without LUDOX (**Fig. 5**). The highest CO<sub>2</sub> conversion and energy efficiency of 15% and 4%, respectively, were obtained for SiO<sub>2</sub>@TiO<sub>2</sub> – 0.25M with LUDOX, being the packing material that shows the most continuous shell of TiO<sub>2</sub> around the SiO<sub>2</sub> spheres. It can be deduced that it is important to have a continuous layer of dielectric material covering the SiO<sub>2</sub> packing material. The enhanced

performance can be ascribed to different aspects which cannot be distinguished, such as the possibility to produce high energy electrons at the contact point of two spheres [62] or the generation of highly active (charged) sites at the surface or differences in discharge mode [39, 63]. Other possible unidentified material effects cannot be excluded at this point. This concurs with the conclusion of Mei et al. who indicated synergy when using titania pellets in the plasma discharge for CO<sub>2</sub> conversion (conversion improved by a factor of 2.5) and attributed this to a combination of physical and chemical effects, including those induced at the photocatalytic surface driven by high energy electrons from the CO<sub>2</sub> discharge rather than the photons in the plasma [37].

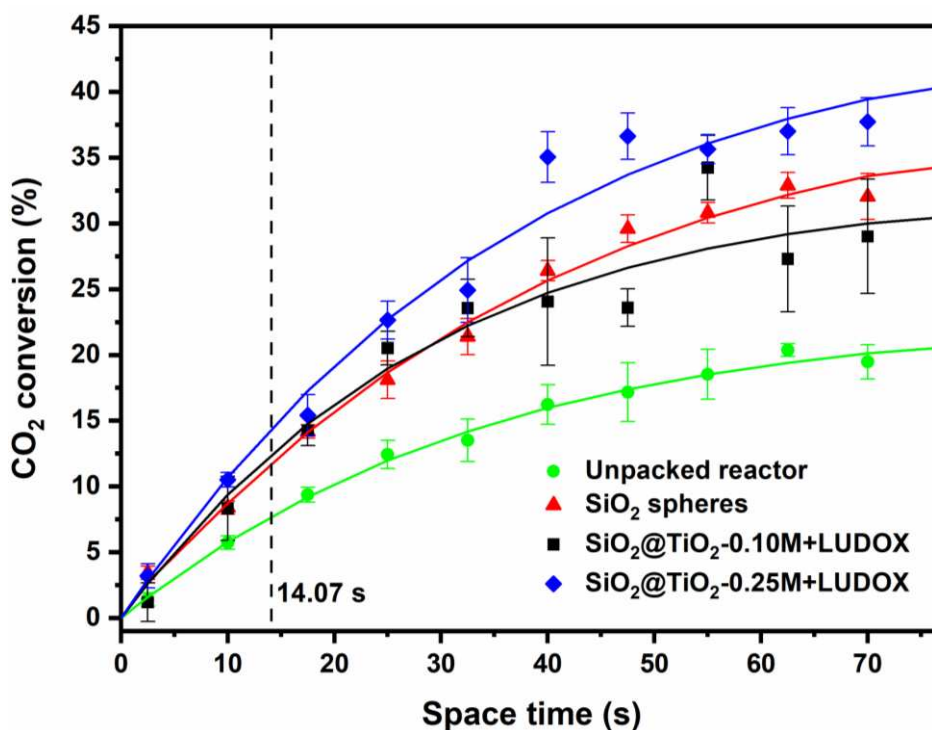


**Figure 5.** Plasma-catalytic activity on core-shell SiO<sub>2</sub>@TiO<sub>2</sub> spheres without LUDOX (a & c) and with LUDOX (b & d) in function of the applied concentration of Ti(IV) precursor during coating of the SiO<sub>2</sub> core material, compared to the unpacked reactor at same flow rate (39 ml/min) and at same space time (14.07 s; flow rate of 75 ml/min).

If the spheres have cracks or a non-continuous layer of  $\text{TiO}_2$ , there is more possibility for contact points between  $\text{SiO}_2$  and  $\text{TiO}_2$  or  $\text{SiO}_2$  and  $\text{SiO}_2$ , which might reduce the number of high energy electrons, which might cause the lower increase in conversion [64].

### 4.3. Effect of space time

The single point measurements presented here, showed an approximate idea of activity at short space time, which is not an ideal condition to make any conclusion on conversion or performance. Therefore, the recommendation towards multipoint-space time measurements for plasma-catalytic reactions, made in previous work and demonstrated on uncoated dense spheres, was followed [11, 31, 57]. Hence, to validate the conversion results at steady-state conditions, the changes in the conversion with respect to space time for  $\text{CO}_2$  dissociation were evaluated at space times ranging from 2.5 to 70 s for an unpacked reactor and a reactor with a packing of  $\text{SiO}_2$ ,  $\text{SiO}_2@ \text{TiO}_2 - 0.10\text{M} + \text{LUDOX}$  and  $\text{SiO}_2@ \text{TiO}_2 - 0.25\text{M} + \text{LUDOX}$  (**Fig. 6**). A constant volume of the catalyst was used in  $\text{CO}_2$  conversion; hence the results presented as a function of space time is also represented in GHSV (**Fig. S5.**)



**Figure 6.** Plasma-catalytic  $\text{CO}_2$  conversion as a function of space time; compared with single-point space time (vertical dashed line).

Increasing the flow rate will reduce the conversion because of the shorter space time and thus contact with the plasma and the packing material. However, with decreasing flow rate, and thus

increasing space time, the conversion increases until a certain point and then becomes more constant for all packed and unpacked reactors. It is clear that with increasing space time, the impact of the different packing materials becomes more pronounced, as was also observed for other packing materials [31]. The space time measurement confirms that the packing material enhances the conversion of CO<sub>2</sub>, proving the packing effect in the plasma reaction.

**Table 2:** Fitted kinetic and partial chemical equilibrium data for the CO<sub>2</sub> splitting reaction, at a plasma power of 30 W and a frequency of 3 kHz, in a 4.5 mm gap size reactor.

samples	k (s <sup>-1</sup> )	X <sub>e</sub> (%)	k <sub>loss</sub> (s <sup>-1</sup> )	f k <sub>form</sub> (s <sup>-1</sup> )
Unpacked reactor	0.032 ± 0.005	23 ± 2	0.007 ± 0.002	0.025 ± 0.006
SiO <sub>2</sub> spheres	0.027 ± 0.002	40 ± 2	0.011 ± 0.001	0.016 ± 0.002
SiO <sub>2</sub> @TiO <sub>2</sub> – 0.10M+LUDOX	0.039 ± 0.009	33 ± 3	0.013 ± 0.004	0.026 ± 0.009
SiO <sub>2</sub> @TiO <sub>2</sub> – 0.25M+LUDOX	0.032 ± 0.004	45 ± 3	0.015 ± 0.003	0.018 ± 0.003

A comparison was made for the activity of core-shell SiO<sub>2</sub>@TiO<sub>2</sub> – 0.10M+LUDOX and 0.25M+LUDOX materials based on the multiple-point measurement. Even though the SiO<sub>2</sub>@TiO<sub>2</sub> – 0.10M+LUDOX packing material exhibited a slightly better conversion at the single point measurement (14.07 s space time), it converted less CO<sub>2</sub> than the packing consisting of bare SiO<sub>2</sub> spheres at longer space times where partial chemical equilibrium is being reached. This suggests that the formation of cracks and exposed SiO<sub>2</sub> surface in the core-shell packing material have a negative effect on the CO<sub>2</sub> dissociation, which could confirm the indicated reduced number of high energy electrons as predicted by simulations [64]. Nevertheless, we cannot exclude other possible occurring mechanisms that might be responsible for the inferior partial chemical equilibrium conversion such as, but not limited to, e.g. diffusion limitations in the coated layer, material boundary and edge effects that influence the discharge, the electric field etc. Moreover, the continuous layer of TiO<sub>2</sub> with less apparent cracks (SiO<sub>2</sub>@TiO<sub>2</sub> – 0.25M+LUDOX) showed the highest CO<sub>2</sub> conversion and energy efficiency (**Fig. S6.**) of 37.7% and 1.8 % at 70 s respectively at the conditions applied here. The highest CO<sub>2</sub> conversion, obtained for SiO<sub>2</sub> and SiO<sub>2</sub>@TiO<sub>2</sub> – 0.10M+LUDOX spheres was 32% and 29% at 70 s, respectively. However, the highest energy efficiency of 4.8% was achieved at 2.5 s for SiO<sub>2</sub>@TiO<sub>2</sub> – 0.25M+LUDOX spheres. At this space time, SiO<sub>2</sub> spheres and SiO<sub>2</sub>@TiO<sub>2</sub> – 0.10M+LUDOX showed energy efficiencies of 4.4% and 1.8 %, although all with a large error on the measurement. The kinetic and partial chemical equilibrium of the CO<sub>2</sub> dissociation using

unpacked and packed reactors are shown in **Table 2**. The fitted reaction coefficient for the CO<sub>2</sub> loss reactions ( $k_{\text{loss}}$ ) increases with a factor of 1.5 from empty to SiO<sub>2</sub> spheres, while the fitted reaction coefficient for the formation of CO<sub>2</sub> reactions ( $f k_{\text{form}}$ ) decreases with a factor of 1.5. This is the reason that overall the global rate coefficient ( $k$ ) stays about the same while the equilibrium is shifted away from CO<sub>2</sub> due to more loss and less formation. Similarly, coating with 0.10 M TiO<sub>2</sub> further increases the loss rate coefficient but apparently also increases the formation term from 0.016 s<sup>-1</sup> to 0.026 s<sup>-1</sup>; perhaps due to some surface effect from the inhomogeneous, cracked TiO<sub>2</sub> layer, possibly promoting the reaction of CO and O<sub>2</sub> back into CO<sub>2</sub>. It caused a decrease in the equilibrium conversion ( $X_e$ ) to 33% and increase in the global rate coefficient to 0.039 s<sup>-1</sup>. That is also the reason why the single-point space time measurements of SiO<sub>2</sub>@TiO<sub>2</sub> – 0.10M+LUDOX seemed better than those of SiO<sub>2</sub> - because of the higher reaction rate coefficient. However, in these multipoint space time measurements the SiO<sub>2</sub>@TiO<sub>2</sub> – 0.10M+LUDOX sample performs worse than SiO<sub>2</sub> because the equilibrium conversion is lower. Lastly, adding more TiO<sub>2</sub> (SiO<sub>2</sub>@TiO<sub>2</sub> – 0.25M+LUDOX) apparently further increases the loss reaction rate to 0.015 s<sup>-1</sup> and lowers the formation rate to 0.018 s<sup>-1</sup>. It shows that an increase in the TiO<sub>2</sub> loading and coverage of TiO<sub>2</sub> layer with less apparent cracks, improves CO<sub>2</sub> splitting and reduces the CO<sub>2</sub> formation reactions. From the multipoint space time measurements, it can therefore be deduced that the introduction of packing materials in the form of core-shell structure as well as the morphology, loading and presence of binders of the coated shell, have a huge impact on the plasma-assisted CO<sub>2</sub> conversion, due to the combination of physical and chemical, surface and bulk properties. Although the data clearly show that these effects change the apparent partial chemical equilibrium ( $X_e$ ) proving a physical and/or chemical effect of the packing material on the conversion process, there is no clear evidence of a catalytic effect. For, although the rate coefficient of SiO<sub>2</sub>@TiO<sub>2</sub>-0.10M+LUDOX seems enhanced, the difference not significant. Moreover, the rate of the loss and formation reaction is not influenced in the same way. Hence, it is difficult to conclude whether a true catalytic effect is present on top of the clear physical/chemical effect.

## 5. Conclusion:

Core-shell SiO<sub>2</sub>@TiO<sub>2</sub> spheres with and without LUDOX were successfully prepared by spray coating aqueous citratoperoxotitanate(IV) precursor solutions at different concentrations, followed by thermal processing. The obtained TiO<sub>2</sub> coatings were shown to exhibit an anatase crystal structure in Raman spectroscopy. From SEM, it was confirmed that at a too high concentration (0.50 M), the TiO<sub>2</sub> partly detaches from the sphere and more cracks and island-

like TiO<sub>2</sub> coatings are being formed. Using 0.1 wt% LUDOX as a binder improves the layer's continuity and reduces cracks and formation of separate TiO<sub>2</sub> island-like structures. Plasma-assisted CO<sub>2</sub> dissociation experiments confirm the impact of surface changes, induced by the preparation condition of the shell and the morphology of the core-shell layer. The maximum CO<sub>2</sub> conversion of 37.7% (at a residence time of 70 s corresponding to an energy efficiency of 2%) and the highest energy efficiency of 4.8% (at a residence time of 2.5 s corresponding to a conversion of 3%) are obtained with SiO<sub>2</sub>@TiO<sub>2</sub> – 0.25M spheres with LUDOX at 30 W, 3 kHz and a 4.5 mm discharge gap. These results confirm that core-shell spheres are promising packing materials to enhance the plasma performance compared to bare SiO<sub>2</sub> spheres and unpacked reactors, when the properties of the shell can be sufficiently controlled. Here, we have adopted a solution-based method to coat mm range spheres and investigated the changes in surface morphology and TiO<sub>2</sub> loading on the core-shell packing materials and their effect in the plasma-catalytic CO<sub>2</sub> conversion. It is clear that materials have a high potential in plasma-based conversion processes, while the impact of material properties on conversion needs more detailed attention.

### **CRedit authorship contribution statement**

**Periyasamy Kaliyappan:** Writing – Original draft preparation, Data curation, Investigation, Conceptualization **Andreas Paulus:** Investigation **Jan D'Haen:** Investigation **Pieter Samyn:** Resource, Writing – review & editing **Yannick Uytdenhouten:** Formal analysis, methodology **Neda Hafezkhiani:** Methodology **Annemie Bogaerts:** writing – review & editing **Vera Meynen:** Writing – review & editing, Conceptualization **Ken Elen:** Writing – review & editing **An Hardy:** Supervision, Writing – review & editing, Conceptualization **Marlies K. Van Bael:** Supervision, Writing – review & editing, Conceptualization

### **Declaration of competing interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

The following is Supplementary data to this article

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