PAPER

Judging the feasibility of TiO₂ as photocatalyst for chemical energy conversion by quantitative reactivity determinants

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In this study we assess the general applicability of the widely used P25-TiO₂ in gas-phase photocatalytic CO₂ reduction based on experimentally determined reactivity descriptors from classical heterogeneous catalysis (productivity) and photochemistry (apparent quantum yield/AQY). A comparison of the results with reports on the use of P25 for thermodynamically more feasible reactions and our own previous studies on P25-TiO₂ as photocatalyst imply that the catalytic functionality of this material, rather than its properties as photoabsorber, limits its applicability in the heterogeneous photocatalytic CO₂ reduction in the gas phase. The AQY of IrO_x/TiO_2 in overall water splitting in a similar high-purity gas-solid process was four times as high, but still far from commercial viability.

Introduction

Within the last decades photocatalysis has attracted lots of attention because it bears potential to contribute to the development of novel strategies for renewable energy sources. TiO_2 is still the most frequently applied semiconductor in a manifold of different reactions, mainly due to its sufficiently wide band gap (>3.0 eV), its availability and its physical and chemical stability.[1] A commercially available TiO_2 composite consisting of approximately 20% rutile and 80% anatase (P25, Evonik Industries) is often considered as the standard or benchmark material in photocatalytic research.[2] One of the most prominent photocatalytic reactions on semiconducting materials is the reduction of CO_2 to CH_4 utilizing H_2O splitting as hydrogen source (eqn (1)).

$$CO_2 + 2H_2O \xrightarrow{hv,\ photocatalyst} CH_4 + 2O_2 \qquad (1)$$
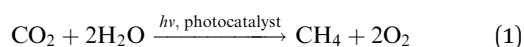
Many groups have carried out important and detailed research on this very complex reaction following the pioneering work of Inoue *et al.*,[3] including mechanistic studies and investigations of the structure–activity relationship,[4–11] effects of co-catalysts, doping, substrates and composites.[12–19] Unfortunately, despite

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years of research on photocatalytic conversion of CO_2 on TiO_2, the exact mechanism of CH_4 formation is still unknown and the formation rates are generally low, ranging from a few nmol g_{cat}^{-1} h^{-1}, especially regarding pure P25-TiO₂, to an order of µmol g_{cat}^{-1} h^{-1} for modified TiO_2-based materials.[2] The tininess of product formation contributes to the complexity of this reaction, as it makes the analytics very difficult and allows only a few techniques, such as highly specialised GCs. Regarding the almost 40 years of high-quality research, the question may arise why it was not possible to achieve a major breakthrough in terms of catalytic efficiency and detailed understanding of CO_2 reduction on the molecular level up to now.

Our groups have also devoted considerable research effort on this research topic with the main focus on carrying out the reaction under high-purity conditions in the absence of carbon-containing impurities. As main conclusions from our work we were able to prove true CH_4 formation from CO_2 as a reactant, although we were never able to detect gas-phase oxygen as a byproduct (eqn (1)) with pure P25-TiO₂ as the photocatalyst.[20–23] The variation of reactant concentration and light intensity revealed that the formation of CH_4 actually results from a photo-induced process on TiO_2 and that maximum CH_4 formation was achieved at low reactant concentrations. We have yet to demonstrate the possibility to obtain quantitative activity determinants under high-purity conditions, enabling a final conclusion on the potential of P25-TiO₂ in photocatalytic CO_2 reduction. In accordance with earlier work[24,25] it seems desirable to apply different quantitative descriptors. The apparent quantum yield, as outlined below, is an appropriate measure to describe the light-based efficiency of the process, but it does not take into account the applied photocatalyst

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quantity. On the other hand, typical measures from heterogeneous catalysis, such as the productivity, do not consider light intensity or light absorption.

The rate of a photocatalytic reaction is strongly influenced by the intensity and energy of the incident light beam, the charge carrier dynamics and the illuminated portion of surface area.[26] As a consequence the validity of comparing rate constants of photocatalysts (at a given temperature and pressure) will be limited. To circumvent this, a generally accepted approximation is to describe the activity of a photocatalyst by regarding the quantum yield (QY).[27] The QY is defined as the ratio between the amount of charge carriers consumed by product formation and the amount of photons absorbed by the photocatalyst (eqn (2)) which consequently excite an electron–hole-pair. These charge carriers will be consumed by the photochemical process, if they escape from recombination and arrive at the active sites on the surface of the photocatalyst where they undergo a charge transfer reaction with an adsorbed reactant.

$$QY = \frac{N_{\text{consumed charge carriers}}}{N_{\text{absorbed photons}}} \tag{2}$$

$$AQY = \frac{N_{\text{consumed charge carriers}}}{N_{\text{incident photons}}} \tag{3}$$

The number of the consumed charge carriers can be directly deduced from the amount of formed products. A calculation of the absorbed photons is only possible if the incident, reflected and scattered photons can be quantified,[26] which is rarely the case. In order to avoid this fundamental problem it became popular to use instead the amount of incident photons.[28–30] A determination of the latter can be performed by an actinometrical measurement of the light source. The ratio between the amount of consumed charge carriers and the amount of incident photons is termed the apparent quantum yield (AQY) (eqn (3)) or apparent photonic yield.[26] AQY as measure for the efficiency of a photocatalyst should be determined in a range where the product formation rate no longer depends on the catalyst mass. This ensures optimum light absorption.[24] However, when considering the term 'efficiency' from the viewpoint of classical heterogeneous catalysis, AQY is not ideal because it does not take into account the applied photocatalyst quantity or the ideal illumination of the latter.[25]

In classical heterogeneous catalysis, the comparison of different catalysts is often performed on the basis of mass-related production rates in μmol g^{-1} h^{-1} as a measure for the productivity of a certain catalyst. For photocatalytic reactions, calculation of this quantity requires that the entire sample mass is exposed to light and thus in principle able to participate in the reaction.

A critical point in the literature dealing with CO$_2$ reduction in both, the QY and the productivity estimation, is the ambiguity if the experiments were performed in absence of carbonaceous impurities. It is important to notice that in reactions with such low product yields particular caution has to be exercised concerning impurities on the photocatalyst, as adsorbates from prior air contact or remains from syntheses can contribute to the products formed during the reaction.[31–33] Thus, it is clear that both determinations are meaningless without adequate purification steps before the CO$_2$ reduction experiment, as products formed from such species overestimate the number of consumed charge carriers and the amount of formed products. Due to an insufficient removal of carbonaceous species, the sensitivity of the photochemical performance of TiO$_2$ to the illumination properties and the diverse approaches of performing QY analysis, it is obvious that the obtained values often differ by orders of magnitude.[34,35]

In this work, both reactivity determinants, the AQY and the productivity, are determined under suitable conditions for each quantity. Thin films deposited on glass surfaces were used to study the effect of the deposited mass on the production of hydrocarbons. We show that all of the deposited titania in these films participates in the photoreaction which allows an accurate determination of the productivity. Due to the low product yields, these experiments had to be performed under batch conditions. Under steady methane formation in continuous flow we show an approach to determine the AQY of powdered bare TiO$_2$ (P25) in the gas-phase photocatalytic CO$_2$ reduction. Furthermore the AQY of IrO$_x$ modified P25 (IrO$_x$/P25) in the gas-phase photocatalytic H$_2$O splitting was analysed under similar flow conditions. For the first time the AQY of both, the CO$_2$ reduction and H$_2$O splitting is determined under exclusion of contaminants in order to ensure a proper analysis of the activity of P25 and IrO$_x$/P25. These numbers can serve as a reference for others.

Based on the results presented here, we strongly suggest that P25-TiO$_2$ is not suitable as photocatalyst for gas-phase CO$_2$ reduction because (i) the reaction is most likely not a full catalytic cycle with the oxygen probably being consumed by titania and (ii) both, productivity and AQY are far below any commercial viability.

Results and discussion

In order to study the effect of the mass of the P25 photocatalyst in CO$_2$ reduction under high-purity conditions, three films were synthesised either by doctor blading (DB) or airbrush technique (AB: air brush; TAB: thick air brush). The latter was employed as it does not require any organic solvents to deposit the P25 particles on the glass surface. The SEM images (Fig. 1) exemplarily illustrate that the TAB film exhibits a rather uniform distribution of the P25 material. This is not the case for the AB sample. In order to produce thinner and more uniform films doctor blading was used. Even though the used paste includes organic solvents, the calcination of the deposited film and the extensive photocatalytic cleaning of the samples inside the reactor ensure that any remaining carbon-containing impurities are successfully removed. In the case of the DB and TAB samples, a calculation of the average film thickness was possible (Table 1). Due to the short airbrush deposition time, the AB film was not uniform exhibiting thicker and thinner domains of deposited P25 (Fig. 1).
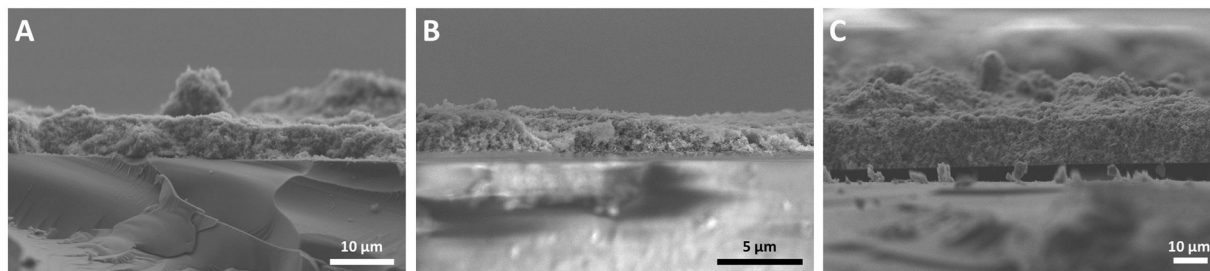
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Fig. 1 SEM images for the three tested films DB (A, left), AB (B, middle), TAB (C, right).

Table 1 Average thickness and deposited mass for the three tested films and calculation of the respective CH_4 yield of photocatalytic CO_2 reduction

Sample	Average film thickness/μm	Mass/ mg	CH_4 yield/ μmol	CH_4 productivity/ μmol g_{cat}^{-1} h^{-1}
DB	5.4	1.6	1.5×10^{-3}	0.103
AB	—	3.5	2.7×10^{-2}	0.861
TAB	19.9	6.5	1.3×10^{-1}	2.227
TiO_2 (P25) powder	—	50.0	3.4×10^{-1}	0.781

Thus, an accurate calculation of the AB film thickness was not possible. Based on the mass of the deposited P25 (Table 1) and the fact that the geometric dimensions were the same for all three films (2.5×2.5 cm), it can be assumed that the average film thickness of the AB sample is higher than that of DB and lower than the one of the TAB film.

Each one of the films was subjected to photocatalytic CO_2 reduction experiments in batch mode. Excessive cleaning took place inside the reactor until the sample was considered sufficiently clean (no or negligibly low amounts of C-containing impurities). The main product formed in all three cases was CH_4 while only traces of ethane were identified for the AB and TAB films. While other studies also report the formation of CO or CH_3OH, we could not identify these species as products. The CH_4 yields for the three tested films are presented in Fig. 2. After the end of the experiments, the deposited P25 photocatalyst was mechanically removed to quantify the respective deposited masses. Under equal conditions, P25 in powder form (50 mg) was tested as a reference (Fig. 2). All results from the batch experiments are summed up in Table 1.

Based on these results, a calculation of the CH_4 productivity (μmol g_{cat}^{-1} h^{-1}) is possible. As it can be seen from Table 1 there is a linear increase in the deposited mass of the three films (approximate ratio of $1:2:4$ DB : AB : TAB) while the CH_4 productivity also increases linearly (Fig. 3). The linear correlation evidences that indeed all of the deposited titania in the three films participates in the reaction.[25] It is expected, though, that after a certain film thickness and consequently deposited mass is reached, the increase in the CH_4 productivity should be marginal or non-existent.[24] Either the reactants CO_2 and H_2O will not be able to reach the lower layers of the film, or scattering and absorption phenomena will hinder the light from irradiating the entire film. The TAB has a much higher
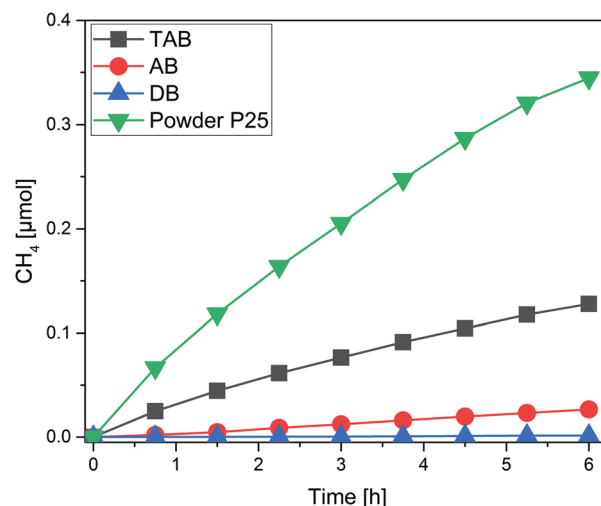

Fig. 2 CH_4 yield for the DB, AB and TAB thin films. P25 powder was used under the same conditions as a reference.

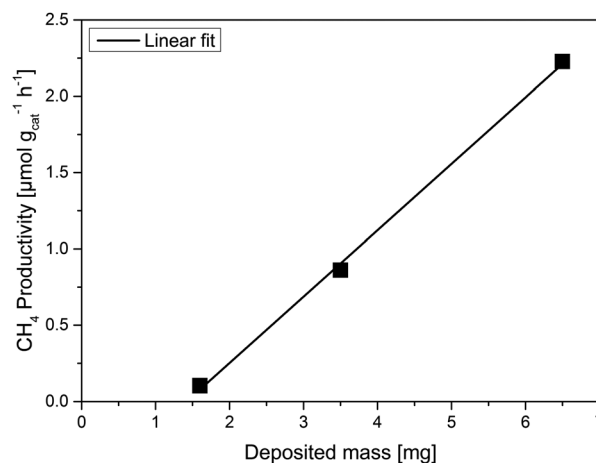**Fig. 3** CH_4 yield for the DB, AB and TAB thin films. P25 powder was used under the same conditions as a reference.

CH_4 productivity than the other three measured samples, including the powder sample with roughly eightfold titania mass. Based on the observed correlation, we can estimate the necessary titania mass of a film to reach the CH_4 yield (μmol) of the powdered P25, amounting to approximately 10 mg on the same 2.5×2.5 cm glass substrate. Thus it is clear that a major

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part of the powdered P25 is inactive in these experiments. The results also show that the mass of all three films is still below a certain threshold where the product yield is independent of the mass of the used photocatalyst. This is not an appropriate basis for the calculation of AQYs.[24]

It should be also noted that no gas-phase O_2 was observed in any of the tested samples, inconsistent with the predicted stoichiometry of eqn (1) but consistent with our previous observations.[20,22]

As in batch mode the reactants and the products of the CO_2 reduction remain in the reactor until the experiment ends, produced CH_4 molecules and other intermediate C-containing species could re-adsorb to the surface of the photocatalyst or react again in further cycles. The adsorbed CH_4 molecules could also facilitate the adsorption or reaction of more CO_2 molecules, thus improving the production of more C-containing molecules.[21] For the aforementioned reasons, it is necessary to perform CO_2 reduction experiments under flow conditions where formed hydrocarbons are continuously removed from the reaction chamber, allowing the calculation of more reliable AQYs. As demonstrated above, the mass of the used P25 will not be relevant, as long as it is above 10 mg. In order to compare the results to our own previous flow mode experiments, we decided to use 70 mg of P25.

The photocatalytic CO_2 reduction with P25 was tested in a combined experiment with two reaction steps. In the first step carbonaceous impurities were removed and in the second step the activity in CO_2 reduction was studied to determine the AQY. Only such a procedure can guarantee that product formation is depending solely on the presence of CO_2. As described in our previous study[20] the detection of CH_4 and CO_2 during the first three hours results from the cleaning procedure. The consistent observation in our previous studies[20,22] was that a residual CH_4 baseline could not be avoided, even after extended cleaning procedures. The only potential reason for this observation not previously excluded is a diffusion of carbonaceous impurities from the bulk of P25. Fig. 4A–C display the result of blank experiments which were conducted to disprove this hypothesis. In all three cases P25 was photocatalytically cleaned for a certain period of time, followed by a dark period to allow diffusion of carbonaceous species from the bulk to the surface, before the photocatalytic cleaning was continued. In the dark

period, the He gas flow of 5 mL min^{-1} was maintained. After the dark period, the illumination was started again, but in contrast to the activity test in Fig. 3 without dosing of CO_2.

The CH_4 formation increases only to the same baseline rate as observed before turning off the illumination (Fig. 4A and B). This result illustrates that no carbonaceous impurities from the bulk are diffusing to the surface of P25 when the light was turned off. Hence, a contribution of impurities from the bulk to the activity in CH_4 formation during the CO_2 reduction experiment in Fig. 3 can be ruled out. Even when pausing the illumination for 18 h, only a slight increase of the CH_4 formation rate can be observed (Fig. 4C).

Regarding the results presented above the CH_4 formed after initiating the photocatalytic CO_2 reduction experiment at 3.75 h (Fig. 5) truly originates from CO_2 as carbon source. A formation of other carbon containing products such as CO, CH_3OH, C_2H_6, C_3H_6, which are frequently mentioned as products of the photocatalytic CO_2 reduction was not observed. Fig. 5 shows that the CH_4 formation rate increased from 3.75 to 6 h. A stable CH_4 formation rate was observed after 6 h. Since the application of the high-purity reactor was essential for this work, the limited interaction between the reactant gas mixture and the solid P25 in the overflow geometry had to be accepted.
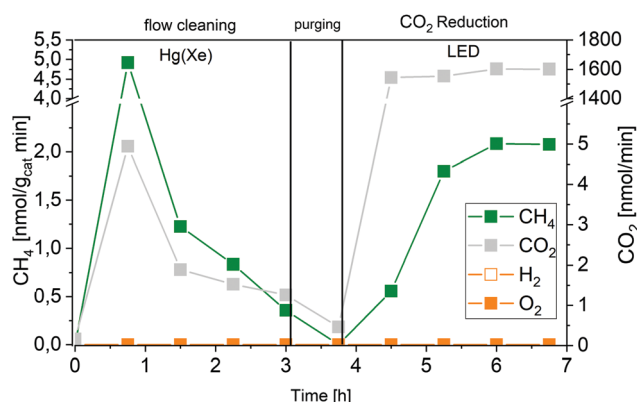
Fig. 5 Approximation of the apparent quantum yield of P25 in the photocatalytic CO_2 reduction. Removal of carbonaceous impurities with Hg(Xe) lamp (0 to 3 h). Purging with He (3 to 3.75 h), no illumination. Photocatalytic CO_2 reduction (3.75 to 6.75 h) with 2 W LED (365 nm).
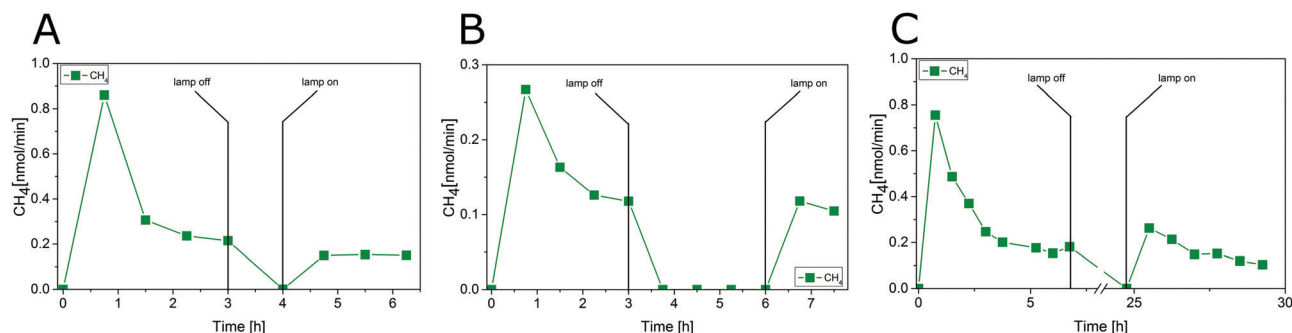
Fig. 4 Removal of carbonaceous impurities with intermediate illumination interruptions, (A) 3 h cleaning, 1 h without illumination, resuming cleaning; (B) 3 h cleaning, 3 h without illumination, resuming cleaning, (C) 6 h cleaning, 18 h without illumination, resuming cleaning.

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As a consequence, the complete mixing of CH_4 in the gas flow to detect a stable formation rate is likely delayed.

The stable formation rate of CH_4 was used as the basis for the AQY determination. The formation of CH_4 from CO_2 requires that two C–O double bonds are cleaved and 4 C–H bonds are formed. In this process eight electrons need to be transferred to the carbon atom. On this account the factor eight was used in the numerator of eqn (4) to obtain the number of electrons from the molar amount of CH_4 formed.

$$AQY_{P25(CH_4)} = \frac{8 \cdot n(CH_4)}{N_{Incident\ photons}} \quad (4)$$

The obtained AQY of 6.5×10^{-4}% in this study implies that only a minimal amount of the energy provided by the illumination source is utilised for the product formation of CO_2 reduction. In Table 2 the value for the AQY of CO_2 reduction is compared with those of other studies dealing with TiO_2. The AQY determined in this study is up to three orders of magnitude smaller (Table 2). A potential reason for this difference can be found in the high-purity conditions of the reactor set-up and the extensive cleaning procedure prior to the activity study. In this way a contribution of products from carbonaceous impurities is avoided. As a consequence the overall amount of CH_4 formed is relatively small, but it can be guaranteed that all of it originates from a reaction with CO_2.

Furthermore, comparing the AQY of CO_2 reduction with studies on thermodynamically more favoured reactions, such as the decomposition of less stable organic compounds on TiO_2, for instance phenol,[36] methylene blue[37] or PCBs[38] shows that the values can reach 1% up to 20%. The fact that the AQY reaches higher values in these reactions when TiO_2 is used as the photocatalyst implies that a significant amount of electrons and holes is available for charge transfer reactions. This indicates that TiO_2 sufficiently functions as photoabsorber and creates charge carriers, but that it is not a suitable catalyst for the formation of CH_4 in gas-phase CO_2 reduction, either because suitable active sites are lacking, or because most charge carriers lack a sufficient thermodynamic driving force to create relevant intermediates.

An additional shortcoming of P25 identified in our previous studies[20–23] is its inability to liberate gaseous O_2 as the stoichiometric byproduct. The often-represented reaction (1) supposes the formation of CH_4 and O_2 in a 1 : 2 ratio. However, under the applied reaction conditions, it was not possible to detect any O_2, although the generation of this product would be an important prerequisite for a complete reaction cycle. The formation of O_2 is often neglected in the literature. It is either

not analysed or cannot be found in the products of photocatalytic CO_2 reduction.[41,42] With some exceptions[8,43–46] the research effort is focused on the formation of carbon related products, since they are the desired products for storing chemical energy.

The absence of O_2 can have various reasons: (i) the consumption of O-derived species in the backward reaction (CH_4 oxidation), (ii) limitations in H_2O oxidation kinetics, so that the reaction stops at adsorbed intermediates, or (iii) the replenishment of defects, namely oxygen vacancies (O_v) on TiO_2.[47,48] This leads to the suggestion that the oxidation half reaction in photocatalytic CO_2 reduction on P25-TiO_2 does not occur. Instead, reactions that consume oxygen take place that are not of catalytic but of stoichiometric nature. Recently, we performed studies on Ir-modified P25 in CO_2 reduction and H_2O splitting. The details are reported in a separate publication,[49] but we would like to mention here, that in contrast to the pure P25 overall H_2O splitting is possible with such a system. Consequently, using IrO_x/P25 gives us the opportunity to comparatively study the AQY of a reaction not limited by a stoichiometric counter reaction.

Fig. 6 demonstrates that IrO_x/P25 shows activity in the overall H_2O splitting reaction. Both products, H_2 and O_2 can be detected in a ratio of almost 2 : 1, according to eqn (5):

$$2H_2O \xrightarrow{h\nu,\ photocatalyst} 2H_2 + O_2 \quad (5)$$
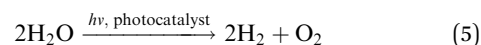
A more detailed analysis of the H_2O splitting experiment in Fig. 6 shows that the O_2 formation rate increases within the first 2.25 h, while the H_2 formation rate is almost stable from the beginning. This observation is a strong indication that a certain amount of evolved O_2 remains on or in TiO_2. The missing amount of O_2 according to the stoichiometric ratio in eqn (5) has been calculated to 410 nmol. Assuming that O_v would be responsible for a complete consumption of the missing O_2 in the H_2O splitting experiment, at least 820 nmol O_v are required. In case of the 70 mg of TiO_2, only ∼0.1% of lattice oxygen positions need to be vacant. On this

Table 2 Comparison of the AQY of photocatalytic CO_2 reduction on TiO_2 from literature und this work

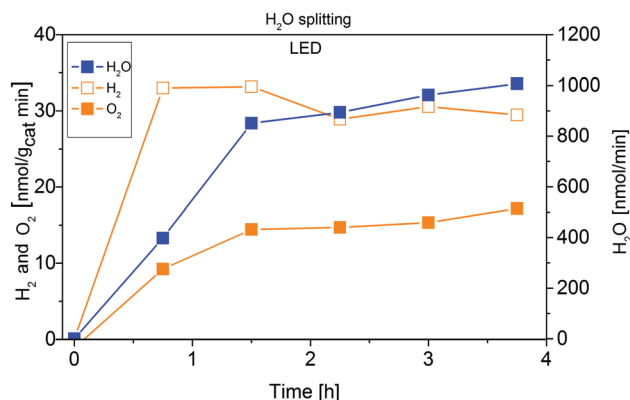| Photocatalyst	AQY/%	Ref.
TiO_2 (anatase)	4.8×10^{-3}	He et al.[39]
TiO_2	1.5×10^{-2}	Yaghoubi et al.[40]
TiO_2 (oxygen deficient)	3.1×10^{-1}	Liu et al.[34]
TiO_2 (P25)	6.5×10^{-4}	This work

Fig. 6 Approximation of the apparent quantum yield of 0.05 wt% IrO_x/P25 in the photocatalytic H_2O splitting reaction. Illumination with 2 W LED (365 nm).

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account, the stoichiometric reaction of surface defects may be an important function in the activity of CO_2 reduction.

Using the stable and stoichiometric values of O_2 and H_2 formation rates, an AQY of $2.5 \times 10^{-3}\%$ is obtained. Although this value is almost four times as high as the AQY of CO_2 reduction, it is still small. It is important to note, that this value has also been obtained under high-purity conditions, so a falsifying influence of carbonaceous impurities acting as sacrificial reagents can be excluded.

To generally achieve higher yields, it may be beneficial to separate reduction and oxidation reaction more rigorously, for example by employing photoelectrochemical processes, Z-scheme systems, or (nano)membrane-based devices. For the case of separate reduction and oxidation sites, using IrO_x as water oxidation catalyst, we already found that CO_2 reduction can no longer proceed simultaneous to water splitting,[49] so more elaborate concepts need to be implemented.

Experimental

All experiments in this work were carried out in two similar high purity photoreactor set-ups described in detail by Mei et al.[50] For the batch experiments, a Shimadzu Tracera GC 2010 plus gas chromatograph equipped with a barrier ionization discharge detector (BID) and a flame ionization detector (FID) was used to quantify CO_2, O_2, H_2O, CH_4 and higher hydrocarbons in the single-digit ppm range, as well as H_2 and CO from ≥ 20 ppm. Illumination in the CO_2 reduction experiments was carried out with a 10 W 365 nm LED (SeoulViOSys), operated at 7.2 V and 0.92 A with a total output intensity of 755 mW cm^{-2} (Thorlabs PM100USB actinometer with a S405C measuring cell).

For the flow experiments, a Shimadzu Tracera GC 2010 Plus, equipped with a barrier discharge ionization detector (BID) was used which allows quantifying CO_2, CH_4, H_2O, H_2 and O_2 in the 0.1 ppm range. A detection of CO, CH_3OH, C_2H_6, C_3H_8 is also feasible. Illumination of the samples for the approximation of the AQY was realised with a 365 nm 2 W high-power LED, operated at 3.5 V and 0.5 A with a total output intensity of 185 mW cm^{-2} (Thorlabs PM100D actinometer with a S305C measuring cell). Monochromatic LED light sources allow a straightforward determination of the incident photons which can be calculated from the light intensity hitting the sample surface. A transmittivity of the reactor lid window of 86% at 365 nm was accounted for in the calculation of the AQY.

Preparation of P25-TiO$_2$ thin films

To remove any loosely bound carbon-containing impurities the P25 powder (Evonik Industries) was calcined in synthetic air at 400 °C for 3 h prior to use. All thin films were deposited on a 2.5×2.5 cm surface of a microscope glass slide. The glass slides were cleaned with a Hellmanex® III cleaning solution, rinsed with de-ionised H_2O and then ultrasonicated for 30 min at room temperature (Elmasonic S 60 H).

For thin films prepared by doctor blading a P25-TiO$_2$ paste was prepared according to Ito et al.[51] with slight modifications. Briefly, 10 mL EtOH were added to a solution of ethyl cellulose (3.5 g, $\sim$50 cP, 10 wt% in EtOH), P25 (0.8 g) and terpineol (6.5 g, mixture of isomers) in a 50 mL round-bottom flask. The mixture was thoroughly sonicated for 45 min at room temperature in an ultrasonic bath (Elmasonic S 60 H). Afterwards, the solvent was removed stepwise with a rotary evaporator (final $T = 40$ °C; final $p = 7$ mbar). The resulting suspension ($\sim$10 wt% P25) was used directly for doctor blading.

For thin films prepared by the air-brush technique, a solution of 0.5 g of P25 in 100 mL de-ionised H_2O was sprayed on the surface of the microscope slides. The glass substrates were put on a hot plate at 250 °C to quickly evaporate sprayed H_2O leaving behind a P25 coating. In order to get films of different thickness, different deposition times were applied.

After deposition, all thin films were calcined at 300 °C for 3 h to increase the adhesion of the powder to the glass surface and to remove the solvents and other C-containing species from the surface of the samples. SEM images of the films were collected using a Merlin VP compact (Zeiss, Oberkochen, Germany). To estimate the amount of deposited P25, the thin films were mechanically removed from the glass substrates after the CO_2 reduction experiments and the received solid was quantified gravimetrically.

Removal of carbonaceous species, photocatalytic CO_2 reduction with P25 and approximation of the AQY

70 mg of P25 were used for the approximation of the AQY in the photocatalytic CO_2 reduction in flow mode. The sample was calcined at 400 °C for 3 h in synthetic air prior to use. After calcination the sample was further cleaned from residual carbon-containing species before the CO_2 reduction was performed. This cleaning step was performed in the photoreactor set-up under continuous flow conditions and at ambient pressure. H_2O enriched He 6.0 (99.9999% He) was flushed (5 mL min^{-1}) through the reactor while a 200 W Hg/Xe light source (Oriel Instruments) irradiated the sample. This polychromatic light source was used in order to clean the sample quickly. A GC measurement was performed every 45 minutes to monitor the cleaning progress. As soon as the concentrations of the products were sufficiently low, the purification step was terminated. After purging out the gas-phase in the reactor, the CO_2 reduction reaction was initiated. The reactant gas, a diluted CO_2 in He mixture (7000 ppm CO_2 in He 6.0) was passed through the reactor with a flow rate of 5 mL min^{-1}.

For the batch experiments, 15.000 ppm CO_2 in He 6.0 and 6000 ppm H_2O filled the reactor up to a final pressure of 1500 mbar. Every 45 min a sample was collected to identify the products of the CO_2 reduction over the course of 6 h. All results were normalised to take into consideration the resulting pressure drop from each sampling event.

Preparation of IrO$_x$/P25 and approximation of AQY in H_2O splitting

The iridium modified sample was prepared by photodeposition in a semi-batch quartz glass reactor. Iridium acetate was used

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as the precursor for the modification of P25. The nominal loading of iridium was set to 0.05 wt%. On-top illumination was realised by a 1000 W Hg/Xe lamp (LOT quantum design). After 3 h of photodeposition, the illumination was stopped. The obtained powder was dried overnight and calcined at 400 °C for 3 h. For the AQY analysis of photocatalytic H_2O splitting, 70 mg of the 0.05 wt% $IrO_x/P25$ were used. Dosing of the reactant H_2O was performed from stainless-steel cups, which are temperature-controlled. The temperature of the saturator was adjusted to set the H_2O concentration in the gas flow to ~ 1000 nmol min^{-1}. The flow rate of the reactant gas flow was also set to 5 mL min^{-1}.

Conclusions

As central outcome of this work, reliable values for AQY and productivity of P25-TiO_2 in photocatalytic CO_2 reduction have been obtained. Thin films composed of less than 10 mg titania are presumably fully illuminated, so that all of the TiO_2 contributes to the product formation and reliable values for the productivity can be obtained. Applying a larger amount of P25 allows determination of reliable AQY values. The resulting values and a comparison with thermodynamically more feasible reactions imply that the absorption functionality of P25 would allow higher yields, but the catalytic function is not suitable for CO_2 reduction reaction. Nevertheless, P25-TiO_2 still represents a valuable material in general photocatalytic research, as it is commercially available and can be used as reference or standard material in other reactions. Implementing the same procedure for overall H_2O splitting with IrO_x/TiO_2 reveals a four times higher AQY value. Additionally, a small amount of O_2 missing in comparison to the expected $2:1$ ratio ($H_2:O_2$) provides further indication that a stoichiometric reaction consuming oxygen species might play an important role in photocatalytic CO_2 reduction.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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