Systematic study of sol-gel parameters on TiO$_2$ coating for CO$_2$ photoreduction

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Graphical abstract

Systematic study of TiO$_2$ properties

UV-Vis: Band gap

PXRD: Phase and crystallinity

Machine vision: Coverage

CO$_2$ Photoreduction

Highlights

- Systematic investigation of TiO$_2$ sol-gel parameters for CO$_2$ photoreduction
- Machine vision to estimate coverage of sol-gel coatings
- Optimisation of sol-gel procedure and benchmarking against P25 TiO$_2$
Abstract An optimized sol-gel method for TiO$_2$ coating was developed for CO$_2$ photoreduction using a systematic Design of Experiments (DOE) approach and an efficient Plackett-Burman (PB) design. Conducting fifteen experiments, the effects of seven sol-gel process parameters were investigated on four catalytic properties for CO$_2$ photoreduction: band gap, catalyst coverage, anatase crystallinity and ratio anatase:rutile. The PB design results yielded a wide range for the catalyst’s properties: band gap (1.86 – 3.35 eV), coverage (11.53 – 99.63%), anatase crystallinity (0 – 48.5 nm) and ratio anatase:rutile (1:0 and 0:1). Machine vision using manual global, Otsu global and adaptive thresholding were compared for estimating the coverage of catalyst on a glass slide support.

Keywords: Design of Experiments; TiO$_2$ sol-gel parameters; CO$_2$ photoreduction; machine vision; photocatalysis

1 Introduction

CO$_2$ photoreduction is a promising route towards lowering CO$_2$ emissions and potentially producing useful chemicals that include CH$_4$ as a fuel.[1, 2] TiO$_2$ and its derivatives have often been used for the photoreduction of CO$_2$ due to its band gap, low cost, availability and chemical stability.[3, 4] The efficiency of CO$_2$ photoreduction using TiO$_2$ can be effected by the catalyst’s properties: band gap [3], crystallinity [3, 5] and ratio of anatase:rutile phases [6]. The band gap of TiO$_2$ prepared by sol-gel has been previously modified using phosphorous dopants [7], nitrogen and fluorine dopants [8], addition of SiO$_2$ to N-doped TiO$_2$ and calcination temperature.[9, 10] The crystallinity of TiO$_2$ particles isolated from sol-gel have been tuned by calcination holding time [11] and calcination temperature. [9, 10, 12-16] The effect of calcination temperature on the ratio of anatase:rutile also has been reported. [9, 10, 17-22]

For the practical application of CO$_2$ photoreduction and flexibility in reactor design, bearing in mind the challenge of dealing with light with directional limitations as an energy source, the catalyst needs to be applied to a support to yield a quality coating. TiO$_2$ coating by sol-gel is attractive, as it requires a simple set up and is relatively low cost. Films of TiO$_2$ have been prepared using sol-gel dip coating and spin coating methods [9, 10, 12, 23-26]. Sol-gel preparation parameters have been previously studied, including amount of water, solvent, acidic hydrolyzing catalyst, high molecular weight co-polymer, calcination temperature and holding time. However, there is no example that includes a detailed investigation of all the parameters used in the preparation of a TiO$_2$ sol-gel on the catalyst’s properties: band gap, crystallinity, ratio anatase:rutile and coating quality. This is most likely the case as sol-gel procedures have several preparation parameters and it would require a large number of experiments to investigate each parameter’s effect on each property. In addition, using published work and consolidating them into a single experiment that yields all of the desired
properties for CO\textsubscript{2} photoreduction is implausible, due to the variation in reagents, catalysts, experimental settings and setups used.

Design of Experiments (DOE) is a powerful tool that allows for generating efficient systematic experimental designs to screen and optimise parameters on selected responses or in this case catalyst properties. DOE is an efficient tool for optimising yield for the synthesis of catalysts and catalytic processes; a variety of examples using full factorial, central composite and Box-Behnken designs are described in the literature.[27-33] The preparation of thin films for novel materials and catalytic processes are challenging, as they require the investigation and optimisation of several process parameters. DOE offers a robust and systematic method for investigating and optimising these coating parameters. A D-optimal design was successfully employed for the development of inkjet printed electrochromic thin films.[34] The effect of parameters for the preparation of TiO\textsubscript{2} thin films: amount acetic acid, water, ethanol, co-polymer Pluronic P123 and calcination temperature on the activity of photodegradation of methyl orange was investigated using a Taguchi method.[35] In another example, the preparation of TiO\textsubscript{2} powder by sol-gel process, a full factorial design was used to investigate the effect of the parameters (amount Titanium tetra-isopropoxide, water, hydrochloric acid and flow feeding rate of reactants) on the mean particle size of calcined TiO\textsubscript{2} isolated.[36]

In this work, a systematic approach using DOE is presented to screen and optimise seven variables: amount isopropanol (IPA), acetic acid, water and polypropylene glycol (PPG), calcination temperature, heating ramp and holding time in fifteen experiments (Table 1). A subset design of DOE, a Plackett-Burman (PB) was used, as it is very efficient at screening four or more parameters in as few as fifteen experiments. To the author's knowledge, this is the first example of a very efficient Plackett-Burman design being used for the process development and investigation of the effect of seven sol-gel preparation parameters on several photocatalytic and physical properties of TiO\textsubscript{2} for CO\textsubscript{2} photoreduction.

2 Experimental

2.1 DOE

Minitab 17 Statistical Software (2010). [Computer software]. State College, PA: Minitab, Inc. (www.minitab.com) was used for creating the experimental design points (Table 1) and analysing the design's responses (Table 2). Minitab was used to model each parameters effect on a response by fitting a

| Table 1: Experiments performed using PB design. For the ratio anatase and crystallinity response, extra experiments were performed to replace the low experimental points from 250 to 400 °C and the three midpoints from 450 to 525 °C. This was done as at 250 °C, no response could be recorded as the resulting sol-gel was amorphous. |
|---|---|
| Sol-gel preparation | Calcination conditions |

3
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<th>Sample name</th>
<th>IPA (ml)</th>
<th>Acetic (ml)</th>
<th>Water (ml)</th>
<th>PPG (ml)</th>
<th>Calcination Temp (°C)</th>
<th>Calcination Rate (°C.min⁻¹)</th>
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<tr>
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<td>0.055</td>
<td>0.3216</td>
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<td>8</td>
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<td>0.6400</td>
<td>3.0</td>
<td>250</td>
<td>15</td>
<td>120</td>
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</table>

Table 2: Experimental results using a PB design for band gap, catalyst on support coverage, crystallinity of anatase and ratio of anatase and rutile phases. "Otsu global thresholding," "Adaptive thresholding and ND = Amorphous material, no data collected by XRD.

Run Order | Sample name | Band gap (eV) | Coverage (%) | Anatase Crystallinity (nm) | Ratio anatase phase ($F_A$) | Ratio rutile phase ($F_R$) |
<table>
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<td>5.08</td>
<td>1.00</td>
<td>0.00</td>
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<tr>
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<td>3.35</td>
<td>98.94**</td>
<td>28.01</td>
<td>0.75</td>
<td>0.25</td>
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<td>67.31†</td>
<td>6.67</td>
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<td>55.74*</td>
<td>0.99</td>
<td>1.00</td>
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<tr>
<td>WT5</td>
<td>3.13</td>
<td>22.55*</td>
<td>16.13</td>
<td>1.00</td>
<td>0.00</td>
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<tr>
<td>WT6</td>
<td>2.70</td>
<td>99.63**</td>
<td>2.06</td>
<td>1.00</td>
<td>0.00</td>
<td></td>
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<td>3.25</td>
<td>18.25†</td>
<td>30.22</td>
<td>1.00</td>
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<td>48.15</td>
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<td>16.23</td>
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<td>WT15</td>
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<td>76.59**</td>
<td>8.45</td>
<td>1.00</td>
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linear function to the parameters under investigation to a response, with Eq. 1 showing a general form of the linear function. The error residual function is shown by Eq. 2.

\[ Y = \beta_0 + \beta_i X_i + \epsilon_i \]  

Eq. 1
\[ \varepsilon_i = y - (\beta_0 + \beta_i x_i) \]  \hspace{1cm} \text{Eq. 2} \\

where:
- \( Y, y \) is the fitted response and actual response values respectively
- \( \beta_0 \) is the y-axis intercept
- \( \varepsilon_i \) is the error residual
- \( x_i \) is the matrix of parameter values, \( n \) is the number of parameters
- \( \beta_i \) is the co-efficient of the parameter calculated form the cost function
- \( i = 1, \ldots, n \) parameters

The parameter coefficients \((\beta)\) and error term \((\varepsilon)\) were determined from a cost function that minimizes the error residual \((\varepsilon)\) between the actual response value and fitted response \((Y)\) by a least squares method \text{Eq. 3}.

\[
\text{Find } \beta_0, \beta_i, \text{ Min } \sum_i^n \varepsilon_i^2 = \sum_i^n (Y_i - y_i)^2 \hspace{1cm} \text{Eq. 3}
\]

Parameters coefficients were significant if the value is shown to be statistically not equal to zero. This was determined by analysis of variance (ANOVA), by calculating the \(p\)-value with the null hypothesis that the parameter coefficient was equal to zero. The null hypothesis was rejected if the \(p\)-value was less than the significance level (alpha, \(\alpha\)). The terms were systematically removed from the linear model starting with the parameter coefficient with largest \(p\)-value. If three or less parameters were significant, the model was converted to a full factorial design, that possibly included interaction terms in the linear model. Interactions are difficult to show experimentally and indicate if parameters effects are influenced by other parameter settings.

The effect of the parameters were investigated on the responses: band gap, coverage, crystallinity and phase ratio of anatase: rutile (Table 2). The models presented were compared to the literature and consolidated to yield a single experimental point using a single coating procedure that yielded a desirable response for band gap, crystallinity, ratio of anatase: rutile and coating coverage. The best design point was further optimized by adjusting the PPG volume equivalents. The use of lower cost lower molecular weights PPG were investigated. The optimized procedure was used to coat stainless steel mesh supports and benchmarked with P25 TiO\(_2\).

2.2 Materials preparation

Isopropanol (IPA, 99.96%) and glacial acetic acid (99.7%) were purchased from Fisher Chemical. Titanium (IV) n-butoxide (99%, Acros), 400, 1000 and 3000 \(\text{g.mol}^{-1}\) polypropylene glycol (PPG, Alfa Aesar) were purchased from the commercial suppliers shown in brackets. The deionized water used was from a Merck Direct-q deionizer.

2.2.1 Preparation of TiO\(_2\) sol-gel
Sol-gel mixtures were prepared using different amounts of chemicals as listed in Table 1. 0.6 ml of titanium (IV) n-butoxide was used for all of the experiments. IPA, titanium butoxide and glacial acetic acid were transferred and agitated together in a sealed sample vial. Deionized water was added in a single step and the vial sealed.

To ensure homogeneity, of at times a viscous mixture, the mixture was agitated for eighty minutes. The mixture was stored in a sealed vial to age overnight. PPG was then added in a single step before being agitated for 40 minutes. Samples were stored in a fridge set at 4 °C for a maximum period of one month, to prevent excessive ageing, before being used to coat a glass strip support. Additional experiments were carried out using the same procedure described above for WT2 (Table 1.) towards testing the effect of molecular weight (400, 1000 and 3000 g.mol\(^{-1}\)) and volume equivalents of PPG on the sol-gel.

### 2.2.2 Coating and calcination

Glass strips (15 of 0.5 mm × 25 mm) were cleaned with dilute sulphuric acid in water (10%), rinsed with deionized water washes (3 × 25 ml) and one IPA wash (25 ml). The glass strips were then dried overnight in an oven at 70 °C. Approximately 2.5 ml of the sol-gel prepared was transferred to a HPLC sample vial. The glass strips were immersed into the sol-gel for one minute before being withdrawn using a dip coater motor set at 50 Hz (Te-Sun Industry Works, Taiwan). The coated glass strips and an aliquot of the sol-gel prepared were calcined as shown in Table 1. For CO\(_2\) photoreduction tests, stainless steel gauge 20 mesh was coated using a similar procedure described above for the glass strips without a dilute sulphuric acid wash.

### 2.3 Sample characterization

#### 2.3.1 UV-vis absorption

The light absorption and electronic band were characterized using a UV-vis spectrometer (Perkin Elmer lambda 950) equipped with a 150 mm integration sphere (Perkin Elmer). The band gap was determined using a direct intercept method (Fig 2) to estimate the adsorption maxima which was then used in Eq. 4.\[37, 38\]

\[
E_g = \frac{h \times \lambda}{C_f} \tag{Eq. 4}
\]

where:

- \(E_g\) is the band gap (eV)
- \(h\) is Planck’s constant \((6.626 \times 10^{-34} \text{ m}^2 \text{ kg s}^{-1})\)
- \(c\) is the speed of light \((3.00 \times 10^8 \text{ m s}^{-1})\)
- \(\lambda\) is the wavelength of adsorption (m)
- \(C_f\) is the conversion factor \(1.6 \times 10^{-19}\)
The coated slides and coverage were analyzed by scanning electron microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDX). A Quanta FEG 650 SEM equipped with Oxford Instruments X-max150 EDX detector and a XL30 LaB6 ESEM equipped with Oxford Instruments X-max 80 EDX detector operated under low vacuum (Typically 0.8 Torr) were used.

### 2.3.3 Crystallinity and phase analysis

Powder X-ray diffraction to determine crystallinity and anatase:rutile phase ratio was performed using a Bruker D8 Advance powder diffractometer, operating with Ge-monochromated Cu K-alpha radiation (wavelength = 1.5406 Å) and a LynxEye linear detector in reflectance mode. Data were collected over the angular range 5-85 degrees in two-theta in one hour. The Debye-Scherrer equation was used to approximate the crystallite size using the half width maximum height of the most intense peak for the anatase and or rutile phase from the XRD pattern and Eq. 5.[39]

\[
D = \frac{K \lambda}{\beta \cos(\theta)} \quad \text{Eq. 5}
\]

where:
- \(d\) is the crystallite size (nm)
- \(K\) is the dimensionless shape factor
- \(\beta\) is the full width at half maximum (FWHM) intensity of the (1 0 1) peak (rad)
- \(\theta\) is Bragg’s diffraction angle (°)

The ratio between anatase and rutile phases was calculated using XRD peak intensity values for anatase and rutile with the Spurr and Myers equation Eq. 6.[40]

\[
f_A = \frac{1}{(1+1.265 \frac{I_R}{I_A})} \quad \text{Eq. 6}
\]

where:
- \(f_A\) is the fraction of anatase phase in the powder
- \(I_A\) and \(I_R\) are the X-ray intensities of the anatase (101) and rutile (110) diffraction peaks, respectively

### 2.3.4 Surface area, pore volume and CO2 adsorption capacity

Samples were degassed under a constant purge of N2 at 200 °C for 10 h. The surface area of the optimised samples were estimated by N2 adsorption isotherms measured at 77 K over forty equidistant points from 0 – 0.95 P/P0 (Gemini VII 2390). The Brunauer, Emmett and Teller (BET) method was used to estimate the surface area from the N2 adsorption isotherms by fitting a straight line to the data collected between 0.05 – 0.3 P/P0.[41] The pore volume was measured at the single point of 0.95 P/P0[41] CO2 adsorption capacities were estimated by the maximum value found from the CO2 adsorption isotherm measured at 273 K over forty equidistant points from 0 to 0.95 P/P0 (Gemini VII 2390).
2.4 CO₂ photoreduction tests

CO₂ photoreduction tests using coated stainless steel gauge 20 mesh were analyzed by an online gas chromatography (GC). A GC (Agilent, Model 7890B series) with a Hayesep Q column (1.5 m), 1/16 inch od, 1 mm id), MolSieve 13X (1.2 m), 1/16 inch od, 1 mm id), thermal conductivity detector, nickel catalyzed methaniser and flame-ionization detector was used to analyze the samples every four minutes. The experimental rig used is shown in Fig 1. A flow rate of 0.063 ml.min⁻¹ CO₂ was sent through a bubbler 20 ±2.0 °C to the reactor overnight to purge the system and saturate the catalyst surface with the reagent gases. The reaction was performed at 36 ±0.1 °C. A UV lamp was used as the light source, light intensity was set at 75 mW.cm⁻² with a wavelength of 365 nm. For comparison to P25 TiO₂, stainless steel gauge 20 mesh was coated with P25 via a slurry deposition of P25 and IPA in an ultrasound bath. The coated mesh was then dried at 150 °C for 2 hours.

3 Results and discussion

3.1 PB design results

3.1.1 Interpreting DOE charts

Pareto charts of standardized effects, main effects and interaction plots are powerful visualization tools that show visually the results of the PB design. Pareto charts of standardized effects indicate the statistically significant parameters as those that are above the red reference line. The weight of the parameters is also indicated by the length of the plotted bar. The main effects plot indicates the parameters effect between high and low settings. The blue circles (Corner point type) on either side of the line is the mean of the values recorded for the high and low settings. The blue line connects these two points. A line with a steep slope indicates the parameter has a strong effect on the response. The red square indicates the mean of the center points (Center point type) – for this study, three replicate points were performed. The grey dotted line indicates the mean for all of the experiments. An interaction plot has similar features to a main effects plot, but includes the presence of an interaction by two intersecting non-parallel lines. The blue solid and green dotted line show the low and high settings effect respectively on the selected parameter shown on the x-axis.
of the graph. The two lines show how at high and low settings, how the setting of the interacting parameter changes its effect on the given response.

![Diagram](image)

**Fig. 1** Experimental rig used for CO₂ photoreduction tests

### 3.1.2 Band gap response

A range of band gaps were recorded for the fifteen PB experiments (**Fig 2**). The PB design was converted to a two factor full factorial design and an interaction effect between calcination temperature and holding time was found (**Fig 3c**). Increasing the calcination temperature resulted in higher band gap values (**Fig 3b**). An increase in the holding time decreased the band gap recorded and had less of an effect relative to calcination temperature (**Fig 3a,b**). The interaction main effects plot shown in **Fig. 3c** showed that at high calcination temperatures, an interaction effect with holding time, where at calcination temperature 650 °C, both 10 and 120 minute hold times yielded the same mean band gap. Whilst at calcination temperature 250 °C, 10 and 120 minute hold times yielded a larger and smaller band gap, respectively. This shows that the dominating effect is that of calcination temperature at high settings, where holding time has little effect as the temperature increases. It is proposed that the change in band gap is from the kinetics of TiO₂ phase change being dependent on temperature at higher calcination temperatures. Momeni *et al* also observed an increase in band gap recorded for N doped TiO₂ films with increasing calcination temperature.[9, 10] The design reported here started with experimental points at 250 °C which
Fig. 2 Representative UV-vis absorption plots for the PB samples that yielded bandgaps between 3.13 – 3.35 eV. The boxed figure is an example of the direct intercept method used to estimate the band gap for WT2. The UV-vis absorption raw data for all fifteen PB experiments can be accessed in the supplementary section.

Fig. 3 (a) Pareto chart of effects showing significance of calcination temperature, holding time and their interaction on the band gap response. (b) Main effects plot showing effect of calcination temperature and holding time. (c) Interaction effect between calcination temperature and holding time.
yielded amorphous TiO$_2$ with low band gap values in the visible light region (≈2.0 eV). At lower calcination temperature (450 °C), the holding time showed a greater difference in effect between short holding times (10 min) versus long holding times (120 min). Longer holding times would encourage increased crystallinity at a set calcination temperature and this has been shown to lower the observed band gap.[11]

3.1.3 Coverage response

Machine vision provides a powerful tool for analysing images.[42] SEM images were taken of the coated glass slides and a Python script was written to perform manual global, Otsu global and adaptive thresholding – see supplementary info for the script used.

The PB design yielded a variety of coatings ranging from poor clumped coatings (Fig. 4a,b) to a thin uniform film, using WT2 settings, with high surface coverage of 98.94% using adaptive thresholding (Fig. 4f). The Otsu method worked the best out of the three Python methods employed as it showed the greatest variation (Otsu $\sigma^2 = 432.67$, Adaptive $\sigma^2 = 227.91$ and Manual $\sigma^2 = 35.15$) and showed the best estimation of coverage when compared by eye with the original images (Table 2). The Python script yielded satisfactory thresholding results, although it must be noted that confirmation of the thresholding still required confirmation by eye.

The amount of water showed the greatest effect on the percentage coverage with an increase in water decreasing the percentage coverage (Fig. 5a,b). Rezaee et al found that for the preparation of yttria-doped zirconia sol-gels, the coating showed more cracking by SEM when excess water was used.[43] Using more water for the preparation of the sol-gels may have caused agglomeration, as water was added in one portion that may have resulted in very fast and complete hydrolysis and polycondensation producing agglomerates. Moemeni et al reported increased cracking with higher calcination temperature and proposed this was due to differences in expansion coefficients between the coating and support used.[9, 10]

Fig. 5d shows that an increase in annealing temperature also increased the crystallinity, as high temperatures could have overcome the surface tension of the coating leading to the formation of cracks. The opposite relationship was found for the amount of PPG used, where the percentage coverage increased with an increase in amount PPG used. Calderon-Morenco et al showed that using high molecular weight polyethylene glycol (PEG) resulted in homogenous films prepared by TiO$_2$ sol-gels.[44] The presence of high molecular weight PEG may have bound the coatings better on calcination as the polycondensed chains were converted to TiO$_2$ crystals.

3.1.4 Crystallinity response

The PB design could be converted to a two factor full factorial design for the crystallinity of the anatase phase response as only one factor, calcination temperature, was found to have a statistically significant effect on the
crystallinity response (Fig. 5c). Amount of PPG was included as it improved the model by increasing the random distribution of residual vs. fitted values. It is potentially an interesting factor to consider in future studies. Again, as per the reasons given when discussing the ratio of anatase to rutile response (Section 3.1.5), the temperature of the low design points and midpoints were taken at 400 and 525 °C, respectively. The experimental design showed an increase in the crystallinity with higher calcination temperature and the amount of PPG used for the preparation of the sol-gel. An increase in calcination temperature has been reported to yield higher TiO$_2$ crystallinity.[9, 10, 12-15]
A variety of coating quality and coverage were observed as a result of the parameter settings shown in Table 1. Adaptive or Otsu global thresholding was chosen by eye by comparing the threshold image with the SEM image. The SEM images are shown on the left and the threshold images on the right. The threshold images include x and y axis in pixel units (a) WT10 (b) WT10 - Otsu global thresholding (c) WT5 (d) WT5 - Otsu global thresholding (e) WT2 (f) WT2 - Adaptive thresholding.

Fig. 5 (a) Pareto chart of effects from full factorial model showing significance of amount of water, PPG and calcination temperature on the % coverage response. No interaction effects were found. (b) Main effects plot showing effect amount of water, PPG and calcination temperature on the coverage response. (c) Pareto chart of effects showing significance of calcination temperature and amount PPG used on the crystallinity of the anatase phase response. (d) Main effects plot showing effect of the calcination temperature and amount of PPG used on the crystallinity response.

The amount of PPG used may have slowed the growth of the crystals and yielded high crystallinity as it has a high affinity with water. This would have slowed down the initial evaporation rate of water. Similar reasons were given by Mosén et al who investigated the effects of polyethylene glycol (PEG) on the crystallinity of spray dried lactose and PEG mixtures.[45] In addition, more PPG could have offered more nucleation sites for the crystallization of TiO$_2$. [45]

3.1.5 Phase ratio response

The PB design showed that the amount of IPA and water used for the preparation for the sol-gel along with the calcination temperature and heating rate were statistically significant effects on the ratio of anatase to rutile phase (Fig. 6a). The results presented use the amount of anatase as a response, if rutile was used the same factors would have been statistically significant and the main effects plots would have been the inverse.
of that shown in Fig. 6b. It can be seen that an increase in the amount of IPA, calcination temperature and heating rate favored a lower ratio of anatase, whilst the opposite was true for the amount of water used (Fig. 6b). The effect of temperature on the phase change from anatase to rutile is well documented.[9, 10, 17-22] It is also worth noting that according to Hanoar et al, the transformation of the anatase to rutile phase is a complex process that could include the following factors: particle size, particle shape (aspect ratio), surface area, atmosphere, volume of sample, nature of sample container, heating rate, and inclusion of impurities.[21] The inclusion of organic crystallization impurities in this work may have resulted from the inclusion of IPA in the crystals formed. Ocana et al showed that the inclusion of organic impurities encouraged the formation of the rutile phase on the catalyst’s surface.[46]

3.2 Optimisation of best design point

3.2.1 Optimal design point

Due to the nature of the wide design space explored for a PB design, there is a high probability that one of the points will yield a useful response. For this PB design, WT2 showed a favorable percentage coverage (98%), band gap (3.35 eV), crystallinity anatase phase (28.01 nm) and anatase : rutile ratio (25:75). WT2’s properties would be of interest to benchmark against the commercially available P25 TiO2 photocatalyst. Using this point’s settings (WT2, Table 1), the effects of PPG molecular weight and volume equivalents were investigated and are presented in the next section.

Fig. 6 (a) Pareto chart of effects showing significance of amount IPA, water and the calcination temperature and heating ramp on the ratio anatase:rutile response. (b) Main effects plot showing effects of IPA, water and the calcination temperature and heating ramp on the ratio anatase:rutile response.

3.2.2 Effect of PPG molecular weight and volume used

Building on the PB design’s results and using the best design point WT2, the coating process was further investigated for the effect of the molecular weight and amount of the PPG used. PPG with molecular weights: 400, 1000 and 3000 were tested. High molecular weight PPG costs more, and therefore, lower molecular
weights were investigated to reduce the cost of the sol-gel preparation. Five volume equivalents PPG relative to the starting volume of titanium (IV) n-butoxide (0.6 ml) was used for the preparation of WT2. To optimise the amount of PPG used, 0.83, 1.66 and 2.50 volume equivalents PPG relative to the starting reagent titanium (IV) n-butoxide were investigated for the preparation of TiO$_2$ sol-gel. When the molecular weight of PPG increased from 400 to 3000, using five volume equivalents PPG, the rutile:anatase ratio increases (Fig. 7). The biggest increase in rutile phase observed for PPG 3000. Some rutile was observed for PPG 1000 and this does warrant further investigation in the future. The anatase crystalline size increased with higher molecular weight (Fig. 7). The mean values recorded for band gap, fraction phase and crystallinity of the anatase phase using 0.83, 1.66 and 2.50 volume equivalents of PPG is shown in Fig. 8. Although a small increase was observed for band gap when increasing volume equivalents of PPG, a one way analysis of variance (ANOVA) indicated that there was no statistically significant difference in means for band gap, anatase phase, rutile phase and crystallinity of anatase phase. The $p$-value ($p$) is the probability that the $F$-statistic ($F$) is larger than the computed test-statistic value. A $p$-value that is more than the significance level ($\alpha$), in this case $\alpha = 0.05$, indicates that the means are not significantly different (Fig. 8). This supports the output from the PB model, where the volume of PPG had no statistically significant effect on these responses.

Fig. 7 Effect molecular weight PPG on: (a) phase fraction (b) crystallinity of anatase phase.
Type IV $N_2$ adsorption isotherms were observed for the TiO$_2$ samples prepared using 0.83, 1.66 and 2.50 volume equivalents of PPG, whilst P25 TiO$_2$ exhibited a Type II adsorption isotherm (Fig. 9a). The type IV adsorption isotherms of the 0.83, 1.66 and 2.50 volume equivalent PPG samples indicated the solids were mesoporous.[47] Type I CO$_2$ adsorption isotherms were observed for the TiO$_2$ samples prepared using 0.83, 1.66 and 2.50 volume equivalents PPG and for P25 TiO$_2$ (Fig. 9b). The samples prepared using 0.83, 1.66 and 2.50 volume equivalents PPG increased $N_2$ and CO$_2$ adsorption compared to P25 TiO$_2$ could be explained by the mesoporous solids yielding a higher surface area versus the microporous P25 TiO$_2$. The surface area and maximum CO$_2$ adsorbed increased with volume equivalents of PPG used (Table 3). CO$_2$ adsorption capacity increased with increasing pressure with a maximum found at 0.95 P/P$_0$ for the TiO$_2$ samples prepared using 0.83, 1.66 and 2.50 volume equivalents PPG, whilst the CO$_2$ adsorption capacity decreased with increasing pressure for P25 TiO$_2$ with a maximum capacity at 0.30 P/P$_0$. For the 0.83, 1.66 and 2.50 volume equivalent PPG samples, an increase in CO$_2$ adsorption capacity correlated with an increase in photocatalytic activity for both CO and CH$_4$ production (Fig. 11). This is likely because a higher CO$_2$ adsorption capacity would increase the probability of CO$_2$ photoreduction as CO$_2$ would be in closer proximity to active sites, especially the (001) anatase facets, on the catalyst's surface.[48]
Table 3: BET specific surface area (SSA), pore volume ($V_{\text{tot}}$) and maximum CO$_2$ adsorption recorded for reference P25 TiO$_2$ and TiO$_2$ catalysts prepared using 0.83, 1.66 and 2.50 volume equivalents PPG.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>SSA (m$^2$/g)</th>
<th>$V_{\text{tot}}$ (m$^3$/g)</th>
<th>Max CO$_2$ adsorption (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P25</td>
<td>53.31</td>
<td>0.090</td>
<td>0.17</td>
</tr>
<tr>
<td>0.83 Vol. eq.</td>
<td>50.01</td>
<td>0.074</td>
<td>0.22</td>
</tr>
<tr>
<td>1.66 Vol. eq.</td>
<td>87.69</td>
<td>0.113</td>
<td>0.36</td>
</tr>
<tr>
<td>2.50 Vol. eq.</td>
<td>111.91</td>
<td>0.118</td>
<td>0.43</td>
</tr>
</tbody>
</table>

3.2.3 CO$_2$ photoreduction results

The reaction was attempted twice as Run 1 and Run 2 using 1.66 equivalents of PPG (Fig. 10). For Run 1 and 2 using 1.66 volume equivalents PPG, similar trends were observed for the production of CO and CH$_4$, with Run 1 producing more CO initially and later matching Run 2’s CO production. This was confirmed with paired two sample t-tests, where if the calculated $t$-statistic is greater than the critical value (cv) of the student’s $t$-distribution table, using the degrees of freedom (df) and significance level ($\alpha$), the means are significantly different. Run 1 and 2 yielded statistically equal CH$_4$ production over the entire time range ($\alpha = 0.05$, df = 142, $t$-statistic = -0.5735, cv = 2.576). Run 1 and 2 yielded statistically equal CO production from 204 minutes ($\alpha = 0.05$, df = 40, $t$-statistic = 0.9016, cv = 2.704). The coated meshes prepared by the sol-gel method were compared to a mesh coated with reference P25 TiO$_2$. For both CO and CH$_4$ production, P25 TiO$_2$ coated mesh performed better (Fig. 11). The difference in performance could be due to the differences in crystallinity and band gap (Table 4). Increase in band gap has been reported with decreasing crystal size, where the rutile
crystallite size for the 1.66 and 0.83 volume equivalents PPG samples having much larger rutile and slightly bigger anatase crystallite sizes compared to P25.[5, 49] The larger band gap and resulting increase in the number of photons generated by P25 would favor CO$_2$ photoreduction.[3] The difference in production could also be due to the difference in coating methods used where the P25 TiO$_2$ was applied to the stainless steel mesh using a slurry coating method versus a dip coating method for the optimised samples. There are examples in the literature that report the influence of carbon impurities introduced during the catalyst’s preparation and/or from the coating procedure on the production of both CH$_4$ and CO. [50-53] Future work would include investigating the effects of the coating procedure on the potential false positive production of CH$_4$ and CO. It is also important to note that this was a benchmarking exercise where the sol-gel process was developed to yield catalyst properties that were benchmarked against P25 TiO$_2$. In addition, although not as efficient as P25, the advantage this sol-gel procedure is its coating flexibility, where it could be potentially applied to different supports on a large scale using a spray paint process. Mesh coated with 1.66 volume equivalents PPG produced more CO and CH$_4$ compared to the mesh coated with 0.83 volume equivalents PPG. This is most likely due to the synergistic effects of rutile and anatase where an increase in rutile phase exhibits improved photocatalytic activity.[6] The 1.66 volume equivalents PPG sample had 18.1% rutile phase and the 0.83 volume equivalents PPG sample had less with 11.8% rutile phase. In addition, the 1.66 volume equivalents sample had a higher CO$_2$ adsorption capacity (0.36 mmol/g) compared to the 0.83 volume equivalents sample (0.22 mmol/g) where a higher probability exists for the reaction to occur if CO$_2$ is adsorbed onto the catalyst’s surface (Table 3).

**Fig. 10** CO$_2$ photoreduction reaction repeat tests using 1.66 volume equivalents PPG for production of (a) CO and (b) CH$_4$
Fig. 11 CO$_2$ photoreduction reaction tests comparing gauge 20 mesh coated with sol-gel using 1.66 and 0.83 volume equivalents PPG for production of (a) CO and (b) CH$_4$.

Table 4: Comparison of band gap, crystallinity anatase and rutile between reference P25 TiO$_2$, TiO$_2$ catalyst prepared using 1.66 and 0.83 volume equivalents PPG.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Anatase crystallinity (nm)</th>
<th>Rutile crystallinity (nm)</th>
<th>Band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P25</td>
<td>12.6</td>
<td>14.2</td>
<td>3.20</td>
</tr>
<tr>
<td>1.66 eq.</td>
<td>16.2</td>
<td>175.1</td>
<td>3.06</td>
</tr>
<tr>
<td>0.83 eq.</td>
<td>17.6</td>
<td>163.6</td>
<td>3.04</td>
</tr>
</tbody>
</table>

4 Conclusions

A systematic approach using a PB design was used to efficiently screen seven sol-gel parameters towards a catalyst coating with a high coverage and useful properties for CO$_2$ photoreduction. It was possible using a DOE methodology to develop a sol-gel procedure that could tune band gap, coverage, crystallinity and anatase:rutile ratio for CO$_2$ photoreduction. Moreover, the PB design yielded similar observations made in several publications in as few as fifteen experiments. The best design point (WT2) was further optimized to use less PPG. The lower activity of the sol-gel prepared catalyst coatings to P25 was likely due to larger crystallite size, lower band gap values and the potential effects of false positives from the different coating procedures used. This PB design and protocols developed could be employed towards a variety of catalyst coatings with a wide range of properties.

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