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Response Surface Methodology Analysis of CO_2 Photocatalytic Conversion in Presence of CH_4 over Nitrogen-Doped Titania Nanotube Arrays

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Recently, in the research of photocatalytic conversion of CO_2, there has been an increasing innovative interest to simultaneously reduce the level of CO_2 emissions and produce valuable products. In this study, highly ordered nitrogen-doped titania (TiO_2) nanotube arrays, fabricated by anodization method, were used for CO_2 reduction in the presence of CH_4. Response surface methodology (RSM) was employed to assess individual and interactive effects of UV light power, CO_2:CH_4:N_2 ratios in feed and distance between the UV lamp and the reactor on CO_2 conversion. A face-centered central composite design (FCCCD) was utilized to optimize the photocatalytic process conditions. The optimal conditions for maximum CO_2 conversion of 41.5 % were determined as 250 W UV light power, 10 % CO_2 initial ratio and 2 cm distance between UV lamp and reactor.

1. Introduction

The major causes of global warming are said to be greenhouse gases such as carbon dioxide and methane. According to the literature, CO_2 exceeds the natural carbon cycle by about 3.9 % (Mikkelsen et al., 2010). The carbon flow between the oceans and atmosphere is considered natural and a yearly excess of CO_2 is added to the cycle by human activities (Collodi and Wheeler, 2010). Therefore, environmental and chemistry researchers always try to find to reduce the pollutant effect of carbon dioxide, with the aim of addressing the global environmental problems as well as supporting vital carbon resources with a new approach. C_1 chemistry addresses important subjects including utilization and conversion of CH_4 and CO_2, but it offers no practical conversion technique. Usually, the direct CH_4 and CO_2 conversion to oxygenated mixtures is not promising from the thermodynamical aspect (Cai et al., 2014).

The most favorable CO_2 reduction method is applied of photocatalysts as noticeable light irradiation or UV reduces it to beneficial compounds on certain conditions. Semiconductor catalysts (including CdS, TiO_2, CeO_2, ZrO_2, NbO_5, ZnO, etc.) are the excitation source for irradiation with separate energy, and CO_2 is reduced by the photo-excited electrons with another reductant compound on the catalyst surface and generate products that can bear energy such as formaldehyde, methanol, carbon monoxide and acetic acid (Lo et al., 2007).

Catalysts are usually used for the direct conversion of CH_4 and CO_2 to valuable products. Kim et al. (2006), used catalysts with different Ni amounts supported on γ-Al_2O_3 through the electron beam radiation to convert the mixture of CH_4:CO_2:He = 1:1:1 into synthetic mixture of H_2/CO. TiO_2 is one of the favorable photocatalyst among several semiconductor metal oxides for the photocatalytic degradation of chemicals and organic dyes as it has multipurpose properties including wide and direct band gap, semiconducting, large binding energy of excitation (Patel et al., 2014). The finding of self-organized titania nanotube arrays by Gong et al. (2001) has opened new avenues in titania research. Research on titania nanotubes have been encouraging due to their ordered geometry and tunable morphologies as well as improved surface area. Titania nanotube arrays have displayed enhanced performance compared to other forms of TiO_2 as electrodes for photocatalysts and dye sensitized solar cells (Zhu et al., 2007). Scholars have tried to

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extend the range of light absorption of titania (TiO_2) from UV to visible light and have added noble metals or nitrogen for improving the photoactivity of titania further (Gui et al., 2014).

Plenty of experiments are required to determine improved conditions covering all the actual factors with all the possible combinations of parameters, which is unfeasible. One approach is the design of experiments that considers several variables to decrease quantity of experiments. In order to optimize all of the affecting parameters, methodology of statistical experimental design was applied by response surface. This technique, also called response surface methodology (RSM), measures the association between the manageable input parameters and the gained response surfaces. In this study, firstly, nitrogen-doped titania nanotube arrays as a catalyst was fabricated by the anodization method and was then employed to convert CO_2 with CH_4 as reductant under under UV irradiation. RSM was utilized to assess individual and interactive effects of parameters including UV light power, CO_2:CH_4:N_2 ratios in feed and distance between UV lamp and reactor on CO_2 conversion. A face-centered central composite design (FCCCD) was utilized to optimize the photocatalytic process conditions.

2. Experimental

2.1 Preparation of photocatalysts

The nitrogen-doped titania nanotube arrays were synthesized by electrochemical anodization of titanium foils. The anodization was performed in a two-electrode configuration with titanium foil as the working electrode and platinum foil as the counter electrode. All anodizations were performed at 24 V for 1.5 h with mild agitation provided by a magnetic stir bar. Resulting in nanotube arrays with an inside diameter ranging from 3 to 50 nm, about 430 nm length and wall thickness ranging from 7 to 29 nm.

2.2 Photocatalytic reaction experiments

The gas phase stainless steel cubic reactor, which has a dimension of 20 cm × 20 cm × 10 cm was equipped with a quartz window. Sheets of the nitrogen-doped titania nanotube arrays were placed in the centre of the reactor. Then the cap of the photoreactor was sealed using gasket and passed the leakage test. The reaction using gaseous feed (CO_2, CH_4 and N_2) occurred in the photoreactor, continuously illuminated by UV lamp, for maximum 9 hr. An optical process monitor (ILT OPM-1D) was used to measure the light intensity. The conversion products were characterized using residual gas analyzer (RGA) and GC.

2.3 Design of experiments and model fitting

The purpose of this study was to determine the functional relationship between three numerical factors, including UV light power (X_1), CO_2:CH_4:N_2 ratios in feed (X_2) and distance between UV lamp and reactor (X_3) based on response surface methodology (RSM) in conjunction with face-centred central composite design (FCCCD). In order to create the design of experiments (DOE), and generate regression model, design expert software (Stat-Ease, Inc. Silicon Valley, USA) was used. Table 1 shows the coded levels and the ranges of the independent variables of experimental design. The CO_2 conversion (Y_{CO2}) is taken as the response.

Table 1: Coded levels and experimental range of the respective independent variables

Variable	Symbols	Levels		
		-1	0	+1
UV light power (W)	X_1	50	150	250
CO_2:CH_4:N_2 ratios in feed (% CO_2)	X_2	10	45	80
Distance between the UV lamp and the reactor (cm)	X_3	2	4	6

3. Results and discussion

3.1 Coded empirical model equations for CO_2 conversion

The results of the experimental runs are summarized in Table 2. According to the conditions of experiments, the carbon dioxide conversion ranged from 14.34 % to 41.52 %. Furthermore, ANOVA was used to justify the adequacy of the models, and the ANOVA for the quadratic model of CO_2 conversion is summarized in Table 3. As shown in this table, the predicted values reasonably well matched the experimental values with *R-squared* of 0.9936 for CO_2 conversion, meaning that 99.36 % of the total variations for CO_2 in the results can be attributed to the independent variables that were investigated. The *p-value* and *F-value* were used to determine the significance of each term at a specified level of confidence. Therefore, the smaller value is, the more significant its corresponding coefficient and the contribution towards the response variable. From the ANOVA, as indicated by the high *F-value,* some of the variables were perceived very significant to the regression model.

Table 2: Experimental design and actual response of the CO_2 conversion

Design points	Point type	Variables in coded levels			Carbon dioxide conversion (%) Y_{CO2}
		UV light power (W) X_1	CO_2:CH_4:N_2 ratios in feed X_2	Distance between the UV lamp and the reactor (cm) X_3	
1	Center	0	0	0	22.5
2	Center	0	0	0	21.4
3	Center	0	0	0	21.5
4	Center	0	0	0	21.3
5	Center	0	0	0	24.1
6	Center	0	0	0	24.1
7	Axial	1	0	0	32.1
8	Axial	0	1	0	16.5
9	Axial	-1	0	0	23.4
10	Axial	0	0	1	22.0
11	Axial	0	-1	0	34.4
12	Axial	0	0	-1	23.5
13	Fact	-1	1	1	14.3
14	Fact	1	1	1	16.7
15	Fact	-1	1	-1	15.3
16	Fact	-1	-1	-1	28.4
17	Fact	1	-1	-1	41.5
18	Fact	-1	-1	1	31.4
19	Fact	1	1	-1	19.3
20	Fact	1	-1	1	37.2

Table 3: ANOVA for the CO_2 conversion as the desired response

Source	Sum of squares	DF	Mean square	F value	Prob > F	Comments
Quadratic	1,039.28	9	115.48	154.56	< 0.0001	significant
X_1	113.16	1	113.16	151.47	< 0.0001	significant
X_2	822.29	1	822.29	1,100.59	< 0.0001	significant
X_3	3.97	1	3.97	5.31	0.0466	significant
X_1^2	39.58	1	39.58	52.97	< 0.0001	significant
X_2^2	4.89	1	4.89	6.55	0.0308	significant
X_3^2	4.61	1	4.61	6.17	0.0348	significant
X_1X_2	19.59	1	19.59	26.23	0.0006	significant
X_1X_3	10.35	1	10.35	13.85	0.0048	significant
X_2X_3	0.74	1	0.74	1.00	0.3443	not significant
Residual	6.72	9	0.75			
Lack of fit	5.76	5	1.15	4.76	0.0778	not significant
Pure error	0.97	4	0.24			
R-squared	*0.9936*	*Adj R-Squared*	*0.9871*			

Figure 1(a) compares the actual response values obtained from experimental work and the predicted response values based on the quadratic model. It also displays that the experimental range of studies is adequately covered by the model. There is adequate correlation to the linear regression fit, with *R-squared* values of 0.9936 for CO_2 conversion. Additionally, as seen in Figure 1(b), the central composite design provides relatively precise predictions over a broad area around the center point. In fact, the standard error plot shows how the variance associated with prediction changes over design space. The final empirical model in terms of coded parameters is given in Eq.1.

$$Y_{CO2} = 22.87 + 3.36X_1 - 9.07X_2 - 0.63X_3 + 3.84X_1^2 + 1.35X_2^2 - 1.31X_3^2 - 1.57X_1X_2 - 1.14X_1X_3 - 0.30X_2X_3 \quad (1)$$

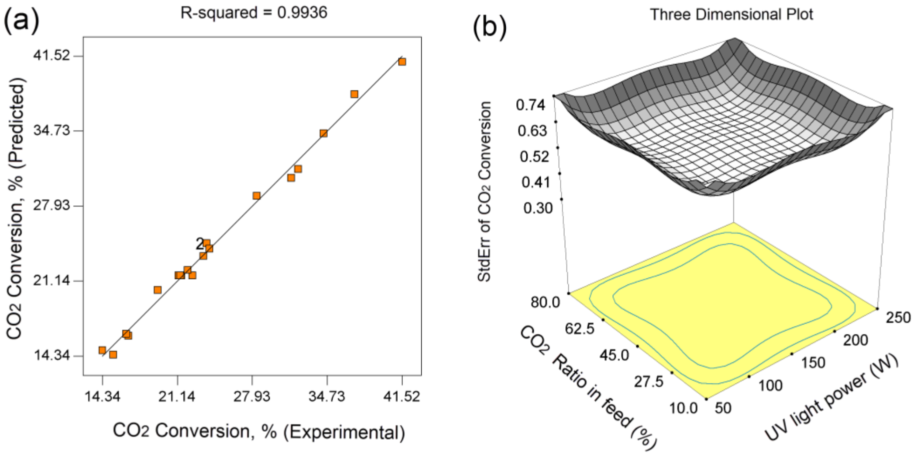

Figure 1: (a) Comparison between the actual response and predicted values for the response of CO_2 conversion and (b) three dimensional standard error plot of CO_2 conversion

3.2 Interactions between process variables

The results in Table 3 show that interactions between variables have significant effect on the photocatalytic conversion of CO_2 over nitrogen-doped titania nanotube arrays. The efficiency of CO_2 conversion is affected by quadratic of X_1^2, X_2^2 and X_3^2, and two way interactions of X_1X_2, X_1X_3 and X_2X_3.

Figure 2(a) shows the effects of different UV light power and CO_2 ratio in feed (i. e. CO_2:CH_4:N_2 ratios in feed) on the CO_2 conversion in three dimensional surface response. From the figure, it is obvious that at any designated quantity of CO_2 ratio from 10 % to 80 %, the photocatalytic conversion of CO_2 proportionally increase with UV light power. In contrast, the photocatalytic conversion of CO_2 increased when the CO_2 ratio in feed was reduced from 80 % to 10 % at any constant UV light power within the range of 50-250 W. The observed phenomenon occurred as increasing the UV light power enhanced the photocatalytic conversion of CO_2. On the other hand, the same trend was not applicable for CO_2 ratio in feed. Although increasing the initial ratio of CO_2 would push this reaction towards producing more products, higher CO_2 stability and limitation of reaction equilibrium would lead to lower conversion (Guo et al., 2009).

The effect of UV light power and distance between the UV lamp and the reactor on the CO_2 conversion at 10 % of CO_2 ratio is shown in Figure 2(b). At low UV light power of 50 W, the CO_2 conversion is marginally affected by distance between the UV lamp and the reactor. However, at higher UV light power, its relevancy to increase CO_2 conversion is enormous. For instance, as can be seen in Figure 2(b), the CO_2 conversion increases steadily at 50 W but when the power was raised to 250 W, the CO_2 conversion escalates significantly to achieve 42.46 % at 2 cm of distance between the UV lamp and the reactor. The UV light power plays an important role in determining the reaction rate in CO_2 conversion as well as yield of photoreduction. For instance, higher UV light power induces faster reaction rate compared to lower UV light power (Cassano and Alfano, 2000). Hence, the optimum UV light power for photocatalytic CO_2 conversion is 250 W as shown in Figure 2(b).

Figure 2(c) represents the effect of interaction between the distance between the UV lamp and the reactor and CO_2 ratio in feed on the CO_2 conversion at constant UV light power of 250 W. Within the studied range of CO_2 ratio in feed, increment in the distance between the UV lamp and the reactor decreased the CO_2 conversion steadily as prolonging the duration did not allow higher reactivity between reactants (Wilcox et al., 2003).

3.3 Process optimization

In order to optimize the photocatalytic conversion of CO_2 over nitrogen-doped titania nanotube arrays, numerical feature of the DOE software was used to calculate the optimum conditions which resulted in maximum conversion. The independent parameters in numerical optimization were set within the range between low and high (I.e. -1, +1) included UV light power, CO_2 ratio in feed and distance between the UV lamp and the reactor, while the CO_2 conversion was set to maximum value. Table 4 presents the constraints of the optimization study. Consequently, for the optimum conditions, the software produced 10 solutions and the solution which was the most desirable was chosen to be verified through three independent experiments. By applying UV light power of 250 W and ratios in feed of 10:80:10, the irradiation intensity passing through the top of the reactor for 2, 4 and 6 cm of distance between the UV lamp and the reactor were 150, 100 and 85 mW/cm^2, respectively. Table 5 tabulates the optimum conditions which coupled with the experimental and predicted values of CO_2 conversion. The experimental average optimum CO_2 conversion of 41 % is well in agreement with the predicted value, with a relative desirability of 0.99, inferring that the model shows high desirability. Since the experimental error is lower than ±5 %, it could be concluded that the suggested statistical model was sufficient to predict the photocatalytic conversion of CO_2 in the presence of nitrogen-doped titania nanotube arrays fabricated by anodization method.

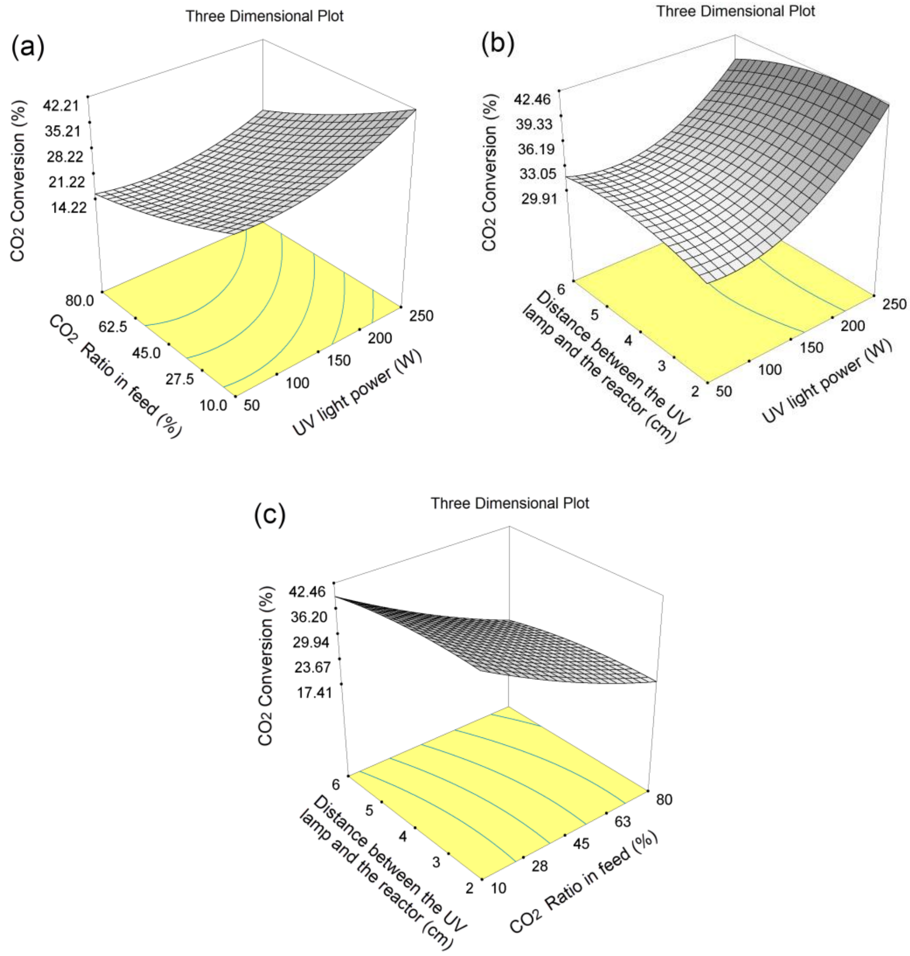

Figure 2: Response surface plot demonstrating the effect of (a) interaction of UV light power and CO_2 ratio in feed and (b) interaction of UV light power and distance between the UV lamp and the reactor (c) interaction of CO_2 ratio in feed and distance between the UV lamp and the reactor on the CO_2 conversion (d) interaction of UV light power and CO_2 ratio in feed on the CH_4 conversion

Table 4: Constraints of variables for the numerical optimization of CO_2 conversion

Variable	Goal	Lower Limit	Upper Limit
UV light power (W)	is in range	50	250
CO_2:CH_4:N_2 ratios in feed (%)	is in range	10	80
Distance between the UV lamp and the reactor (cm)	is in range	2	6
CO_2 conversion (%)	maximize	14.34	41.52

Table 5: Results of independent experiments to validate model adequacy

Run	X_1 (W)	X_2 (% CO_2)	X_3 (cm)	Predicted (%)	Experimental (%)
1	250	10	2	41.5	41.5
2	250	10	2	41.5	41.1
3	250	10	2	42.5	40.4

4. Conclusions

The application of DOE and RSM was demonstrated for optimization of process variables for CO_2 photocatalytic conversion in the presence of CH_4 over nitrogen-doped titania nanotube arrays. Model evaluation and statistical analysis revealed that the RSM can efficiently improve process variables and the predicted values were in accordance with the experimental ones. The effect of parameters such as UV light power, CO_2:CH_4:N_2 ratios in feed and distance between UV lamp and reactor on the conversion were investigated. Optimum experimental conditions indicated that the maximum CO_2 conversion can reach up to 41.5 %. The mathematical model developed was validated and proven to be statistically acceptable and accurate to predict the optimal conversion of photocatalytic conversion.

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