

# 1           **Post-plasma catalytic removal of methanol over Mn-Ce** 2           **catalysts in an atmospheric dielectric barrier discharge**

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24

25 **Abstract:**

26 A post-plasma catalysis system has been developed for the removal of methanol over Mn-Ce oxide  
27 catalysts with different Mn/Ce molar ratios at low temperatures. The Mn<sub>50</sub>Ce<sub>50</sub> oxide catalyst  
28 (Mn/Ce=1:1) shows the best performance in terms of methanol removal efficiency and energy  
29 efficiency of the plasma-catalytic process. The maximum methanol removal efficiency of 99.8% can  
30 be achieved at a discharge power of 16.5 W, while the highest energy efficiency of the plasma-  
31 catalytic process is 47.5 g/kWh at 1.9 W. The combination of plasma and Mn-Ce catalysts  
32 significantly reduces the formation of major by-products (methane, formaldehyde and formic acid)  
33 based on the Fourier transform infrared spectra. Possible reaction mechanisms and pathways of the  
34 post-plasma catalytic removal of methanol are also proposed. A three-layer back propagation artificial  
35 neural network (ANN) model has been developed to get a better understanding of the roles of different  
36 process parameters on methanol removal efficiency and energy efficiency in the post-plasma catalytic  
37 process. The predicted data from the ANN model show a good agreement with the experimental  
38 results. Catalyst composition (i.e. Mn/Ce ratio) is found to be the most important factor affecting  
39 methanol removal efficiency with a relative importance of 31.53%, while the discharge power is the  
40 most influential parameter for energy efficiency with a relative weight of 30.40%. These results  
41 indicate that the well-trained ANN model provides an alternative approach for accurate and fast  
42 prediction of the plasma-catalytic chemical reactions.

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44 **Keywords:** Plasma-catalysis, dielectric barrier discharge, methanol removal, artificial neural  
45 network, environmental clean-up

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## 51 1. Introduction

52 Volatile organic compounds (VOCs) emitted by human activities are one of the major sources  
53 for the formation of photochemical smog and haze [1]. Due to their negative effects on both the  
54 environment and human health, air pollution of VOCs has become a global environmental issue.  
55 However, conventional technologies, such as adsorption, absorption, thermal catalytic oxidation and  
56 combustion, are not cost-effective when dealing with dilute VOCs in high volume gas streams [2].

57 Over the past decades, non-thermal plasma (NTP) technology has been considered as an  
58 attractive and promising alternative for the removal of a wide range of VOCs at atmospheric pressure  
59 and low temperatures [3]. A hybrid technology combining the use of non-thermal plasma with  
60 catalysis, known as “plasma-catalysis”, has gained increased attention to overcome the disadvantages  
61 of NTP processes such as the formation of hazardous by-products. The synergistic effect resulting  
62 from the interactions between the plasma and catalysts can lower the operating temperature of  
63 catalytic reactions, improve the decomposition of environmental pollutants and change the selectivity  
64 of the plasma process to minimize unwanted by-products, as well as enhance the energy efficiency  
65 of the plasma process [4].

66 Plasma-catalysis technology has been demonstrated to be promising for the removal of a wide  
67 range of dilute VOCs in waste gas streams [5]-[11]. Mn-based catalysts have been widely used in  
68 plasma-catalytic processes especially in the post-plasma catalysis configuration due to their ability to  
69 efficiently decompose ozone at ambient temperature. This leads to the formation of reactive oxygen  
70 species for further oxidation of residual pollutants in the effluent, and consequently increases the  
71 removal efficiency of VOCs. Jarrige et al. reported that the combination of a pulsed corona discharge  
72 with  $\text{MnO}_x\text{-Al}_2\text{O}_3$  post-treatment improved the removal efficiency of propane (200 ppm) by over 40%  
73 at a specific energy density (SED) of 200 J/L, while the yield of  $\text{CO}_2$  was 15% higher than that using  
74 plasma alone [12]. Li et al. found that the removal of acetaldehyde was enhanced by over 20% in the  
75 presence of  $\text{MnO}_2/\gamma\text{-Al}_2\text{O}_3$  compared to that using plasma alone at the SED of 8 J/L, while  $\alpha\text{-MnO}_2/\gamma\text{-}$   
76  $\text{Al}_2\text{O}_3$  catalyst exhibited the best activity among all tested catalysts [13]. Cerium oxide ( $\text{CeO}_2$ ) is

77 known as a good promoter for Mn-based catalysts due to its oxygen storage capacity (OSC). Mn-Ce  
78 oxides have shown excellent activity in thermal-catalytic processes such as selective catalytic  
79 reduction of NO<sub>x</sub> and catalytic oxidation of VOCs [14][15]. The addition of Ce to MnO<sub>x</sub> can enhance  
80 catalyst performance due to the increased surface area and Mn dispersion, and higher reducibility  
81 with the involvement of surface oxygen species in reactions [16][17]. However, very limited work  
82 has been carried out using Mn-Ce catalysts in plasma-catalytic oxidation of VOCs [18]. In addition,  
83 previous works were mainly focused on the plasma-catalytic removal of low concentration (10-1000  
84 ppm) gas pollutants in high volume waste streams, while the destruction of VOCs with higher  
85 concentration (e.g. several thousand ppm) using plasma-catalysis is more challenging and has  
86 attracted considerable interest from industry, especially the industry in China due to serious  
87 environmental pollutions. Removal of dilute methanol of either low or high concentration over Mn-  
88 Ce catalysts in a plasma-catalysis system has not been reported before.

89 Plasma-catalysis is a complex process and the reaction performance of the process is controlled  
90 by a wide range of process parameters [18]-[22]. Most of the previous work has mainly focused on  
91 experimental investigations to evaluate the effect of individual process parameters on the plasma  
92 reaction performance [7][23], while a fundamental understanding of the contribution of each factor  
93 and the interaction of different factors to plasma-catalytic reactions is almost nonexistent, making it  
94 difficult to optimize the process parameters and predict the plasma reaction performance theoretically.  
95 Numerical modeling of plasma-assisted VOC decomposition has been proposed to solve this problem  
96 [24][25]. Aerts et al. developed a global kinetic 0D model which consisted of 113 species (electrons,  
97 atoms, ions and molecules) and 1639 reactions, even without a catalyst to investigate the removal of  
98 ethylene in an air dielectric barrier discharge reactor [26][27]. However, although model calculations  
99 can be fast, depending on the type of model, the development of a comprehensive model takes time,  
100 and is thus not always desirable for the fast and cost-effective prediction and optimization of highly  
101 complex and non-linear plasma processes. A recent review article has pointed out that it is still a

102 challenge to develop a comprehensive model involving plasma physics, plasma chemistry and surface  
103 science to deal with the entire plasma-catalytic process [25].

104 Artificial neural networks (ANNs) are considered as a promising tool for process modeling and  
105 optimization. Due to their ability of self-learning, modeling and prediction, ANNs are able to  
106 reproduce a mapping of the input and output variables based on limited experimental samples with  
107 sufficient process units (neurons). As a data-driven model, ANNs are able to predict the performance  
108 of complex processes, which are often not represented by mathematical formulas. More importantly,  
109 less time is needed for the training and optimization of the ANN model [28]. The developed and well-  
110 trained ANN model can precisely predict the output performance of complex nonlinear systems as a  
111 function of suitable input variables. Such a mapping can subsequently be used to predict desired  
112 outputs as a function of suitable input variables, even out of the trained regions. For example,  
113 multiple-layer ANNs have been used for forecasting a wide range of industrial processes such as the  
114 prediction of electrical demand for the national grid. However, there are very few studies on the  
115 application of ANNs in the simulation and prediction of plasma chemical reactions, especially  
116 plasma-catalytic processes [29][30].

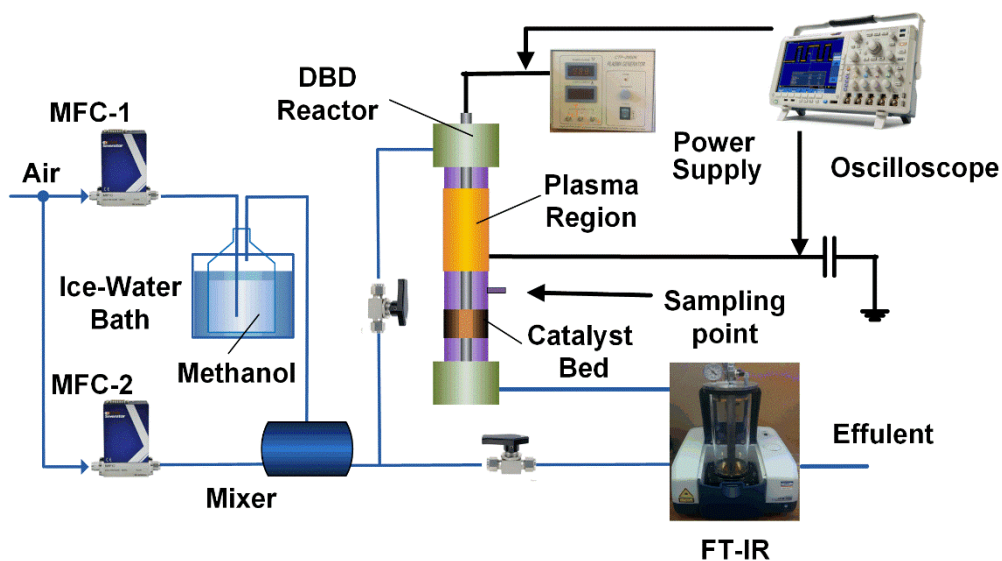
117 In this work, methanol is chosen as a model environmental pollutant since it is a toxic and  
118 volatile alcohol that has been widely used industrially as a solvent, pesticide, and alternative fuel  
119 source. Inhalation or ingestion of methanol may result in blurred vision, headache, dizziness, and  
120 nausea. A post-plasma catalytic process has been developed for the removal of dilute methanol over  
121 the Mn-Ce catalysts with different Mn/Ce molar ratios. The effect of a wide range of plasma process  
122 parameters including the discharge power, Mn percentage, gas flow rate and initial methanol  
123 concentration on the reaction performance has been investigated in terms of methanol removal  
124 efficiency and energy efficiency of the plasma-catalytic process. Possible reaction mechanisms and  
125 pathways involved in the plasma-catalytic process are discussed and proposed based on the identified  
126 gas products. A well-trained back propagation (BP) artificial neural network model has been  
127 developed for the modeling of the post-plasma catalytic process to get new insights into the effect

128 and relative importance of different plasma process parameters on the plasma reaction performance  
129 and to predict the post-plasma catalytic processing of methanol in terms of methanol removal  
130 efficiency and energy efficiency.

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## 132 2. Materials and methods

### 133 2.1 Experimental Setup



134

135 **Fig. 1.** Schematic diagram of the experimental setup

136

137 The experiment was carried out in a coaxial dielectric barrier discharge (DBD) reactor, as shown  
138 in Fig. 1. A 60 mm-long aluminum foil (ground electrode) was wrapped over a quartz tube with an  
139 inner diameter of 8 mm and wall thickness of 1 mm. A stainless steel rod with an outer diameter of 4  
140 mm was placed in the quartz tube and acted as a high voltage electrode. As a result, the discharge  
141 volume was 2.26 cm<sup>3</sup>, while the residence time of the mixture gas was 0.14 s at an air flow rate of 1  
142 L/min. The reactor was connected to an AC power supply with a maximum peak voltage of 30 kV  
143 and frequency of 10 kHz. Air was used as carrier gas (BOC, zero grade, moisture less than 5 ppm),  
144 while methanol (Alfa Aesar) was introduced into the DBD reactor by passing a dry air flow (10  
145 mL/min) through a bubbler kept in a thermostatic ice-water bath (0 °C). High concentration of  
146 methanol (1500-4500 ppm) was chosen for the modeling of the ANN. All gas streams were premixed

147 prior to the DBD reactor. An online power measurement system was used to monitor and control the  
148 discharge power (P) of the DBD reactor in real time. The discharge power of the DBD was calculated  
149 using Lissajous method [31]. The gas temperature in the center of the discharge area was measured  
150 by using a fiber optical thermometer (Omega, FOB102). The maximum gas temperature in the DBD  
151 was less than 150 °C.

152

## 153 **2.2 Catalysts preparation and characterizations**

154 Mn-Ce oxide catalysts with different Mn contents were synthesized using the citric-acid method  
155 [8]. Desired amount of manganese nitrate, ceria nitrate and citric acid (Alfa Aesar) were dissolved in  
156 deionized water. The stoichiometric ratio of citric acid to metal salts was 1.5. The obtained solution  
157 was vigorously stirred at room temperature for 2 h. After that, the solution was stirred in a water bath  
158 at 80 °C to get wet gel, followed by further drying overnight at 110 °C and calcination at 500 °C for  
159 5 h. Pure manganese oxide and ceria oxide were prepared in the same way. All catalysts were denoted  
160 as  $Mn_xCe_{100-x}$ , where x is the molar percentage (%) of Mn. All the samples were sieved to 35-60  
161 meshes. The catalyst pellets (100 mg) were packed into the discharge gap at 50 mm downstream of  
162 the plasma zone, as a post-plasma catalysis configuration. There is no extra heating for the catalyst  
163 bed.

164

## 165 **2.3 Gas analysis**

166 Gas compositions before and after the catalyst bed were analyzed using a Fourier transform infra-  
167 red (FTIR) spectrometer (Jasco FTIR-4200) with a resolution of 2  $cm^{-1}$ . The FTIR spectrometer was  
168 equipped with a 1-16 m variable gas cell (PIKE Technologies), while the effective path length used  
169 in this study was 5.3 m. Measurements were carried out after running the plasma reaction for about  
170 40 minutes, when a steady-state was reached. All experimental data were obtained by averaging 128  
171 scans and repeating 3 times, with the average value of the three measurements being presented.

172

173 The removal efficiency (RE) of methanol (CH<sub>3</sub>OH) is defined as:

$$174 \quad \eta_{\text{CH}_3\text{OH}} = \frac{c_{in} - c_{out}}{c_{in}} \times 100\% \quad (2)$$

175 where  $c_{in}$  and  $c_{out}$  are the methanol concentrations in the untreated gas and effluent, respectively.

176 The energy efficiency (EE) for the removal of methanol in the plasma-catalytic process can be  
177 defined as:

$$178 \quad EE \text{ (g/kWh)} = \frac{M_{\text{CH}_3\text{OH}} \cdot \eta_{\text{CH}_3\text{OH}} \cdot c_{in} \cdot Q}{P \cdot V_m} \times 3.6 \times 10^6 \quad (3)$$

179 where  $M_{\text{CH}_3\text{OH}}$  is the molecular weight of methanol (*g/mol*),  $Q$  is the total gas flow rate (*L/min*),  $P$  is  
180 the discharge power (*W*), and  $V_m$  is the molar volume (*L/mol*).

181

## 182 **2.4 Artificial neural network**

183 A three-layer (input, hidden and output layers) ANN model has been developed for the modeling  
184 and prediction of the plasma-catalytic removal of methanol by using MATLAB neural network  
185 toolbox. Four key process parameters: discharge power, total gas flow rate, initial methanol  
186 concentration and catalyst composition (Mn percentage) are identified as the input variables of the  
187 ANN, while methanol removal efficiency and energy efficiency of the process are used as the output  
188 variables. Therefore, the input and output layer consist of 4 and 2 neurons, respectively.

189 The experimental samples were split into two groups: an input group (X) and a target output  
190 group (T). 70 sets of experimental data were randomly divided into training (70%), validation  
191 (~15.7%) and test (~14.3%) groups; each contains 49, 11 and 10 data sets, respectively. The ANN  
192 model learns by manipulating the connection weights. The weights are adjusted to minimize the mean  
193 square error (MSE) and standard deviation error (SDE). Each network topology was trained for 20  
194 times to counteract the effect of random weights initialization of the network.

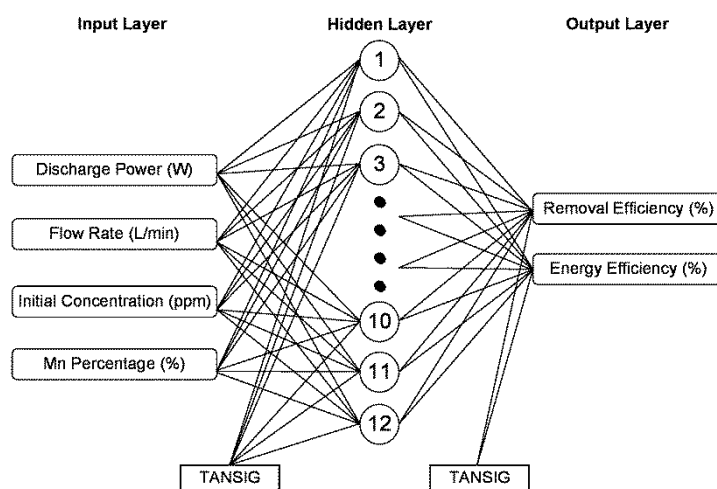
195 BP training algorithm is one of the most popular supervised learning algorithms for the training  
196 of feed-forward ANN [30]. The combination of Levenberg–Marquardt (LM) training algorithm with



197 a TANSIG transfer function at both the hidden and output layers (TT) is chosen for the ANN due to  
198 its best accuracy among the tested cases using orthogonal experiments (see Table S1 in Supporting  
199 Information).

200 The optimal neuron number at the hidden layer was determined to be 12 as the minimum training  
201 error was obtained (see Fig. S1 in Supporting Information). The optimized configuration of the ANN  
202 for plasma-catalytic methanol decomposition is shown in Fig. 2. Finally, the validation of ANN model  
203 shows a perfect agreement between the predicted and experimental results with a correlation  
204 coefficient ( $R^2$ ) of 0.99662 (Fig. S2 in Supporting Information).

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**Fig. 2.** Optimized three-layer ANN model

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### 210 3. Results and discussion

#### 211 3.1 Catalyst characterization

212 The material characteristics of the fresh catalyst samples are listed in Table 1. Compared to the  
213 specific surface area ( $S_{\text{BET}}$ ) of  $\text{MnO}_x$  ( $15.0 \text{ m}^2 \text{ g}^{-1}$ ) and  $\text{CeO}_2$  ( $23.8 \text{ m}^2 \text{ g}^{-1}$ ), the combination of Mn  
214 and Ce species resulted in the formation of a large specific surface area ( $46.5 \text{ m}^2 \text{ g}^{-1}$  to  $88.9 \text{ m}^2 \text{ g}^{-1}$ ) of  
215 the Mn-Ce catalysts, which could provide more active sites on the catalyst surface for the oxidation

216 of methanol. The Mn<sub>50</sub>Ce<sub>50</sub> catalyst has the highest S<sub>BET</sub> of 88.9 m<sup>2</sup> g<sup>-1</sup>, while further increasing the  
217 amount of Mn or Ce resulted in a decrease of the S<sub>BET</sub> of the Mn-Ce catalysts.

218 Fig. 3 shows the XRD patterns of the fresh catalysts. For the MnO<sub>x</sub> catalyst, typical diffraction  
219 peaks of Mn<sub>2</sub>O<sub>3</sub> phase (JCPDS 78-0390) can be clearly observed. The XRD spectra of the CeO<sub>2</sub> and  
220 Mn-Ce catalysts show a typical diffraction pattern of cubic fluorite-type oxide structure (JCPDS 34-  
221 0394). No obvious peaks of manganese oxides are observed in the Mn<sub>50</sub>Ce<sub>50</sub> and Mn<sub>25</sub>Ce<sub>75</sub> samples,  
222 which might be attributed to the effective dispersion of manganese oxides on the catalyst surface or  
223 the incorporation of Mn species into CeO<sub>2</sub> lattice. Further increasing the Mn content leads to the  
224 formation of bulk Mn<sub>3</sub>O<sub>4</sub> (JCPDS 024-0734) and Mn<sub>2</sub>O<sub>3</sub>, which can be confirmed by the diffraction  
225 peaks in the XRD pattern of the Mn<sub>75</sub>Ce<sub>25</sub> catalyst. Moreover, the introduction of Mn into CeO<sub>2</sub>  
226 results in broad diffraction peaks, indicating the formation of the amorphous structure and smaller  
227 crystalline size of the catalysts, which favours the removal of methanol.

228

229

**Table 1.** Material properties of Mn-Ce catalysts

Sample	Specific surface area (m <sup>2</sup> g <sup>-1</sup> )	Total pore volume (cm <sup>3</sup> g <sup>-1</sup> )	Average pore size (nm)
MnO <sub>x</sub>	15.0	0.049	8.35
Mn <sub>75</sub> Ce <sub>25</sub>	71.0	0.144	5.99
Mn <sub>50</sub> Ce <sub>50</sub>	88.9	0.222	4.76
Mn <sub>25</sub> Ce <sub>75</sub>	46.5	0.201	6.17
CeO <sub>2</sub>	23.8	0.106	7.62

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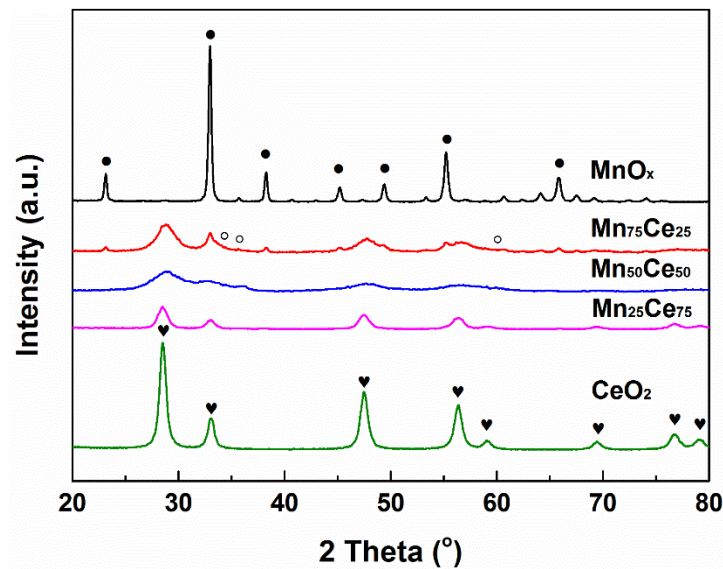


Fig. 3. XRD patterns of Mn-Ce catalysts.

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## 236 3.2 Plasma-catalytic removal of methanol

### 237 3.2.1 Effect of discharge power

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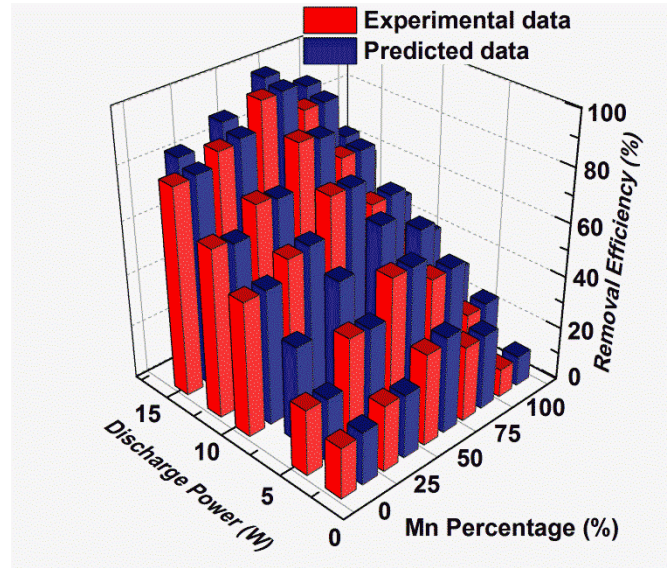
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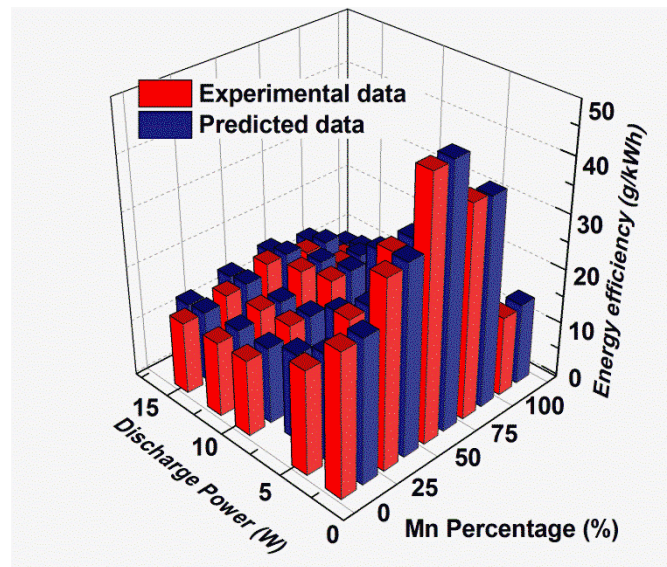
Fig. 4 shows a comparison between the experimental and predicted results for the plasma-catalytic removal of methanol over different Mn-Ce catalysts in the discharge power range of 1.9 - 15 W. The simulated results obtained from the ANN model are in good agreement with the experimental data. The discharge power significantly influences the reaction performance of the plasma-catalytic removal of methanol regardless of the catalysts used. Taking the  $Mn_{50}Ce_{50}$  catalyst as an example, methanol removal efficiency increases almost linearly from 34.6% to 95.4% with the increase of the discharge power from 1.9 W to 15.0 W, as shown in Fig. 4a. The well-trained ANN model could predict the performance of the plasma-catalysis system under other operating conditions. For example, the predicted methanol removal efficiency at the discharge power of 7.0 W and 16.5 W is 65.4% and 97.8%, respectively. In contrast, increasing the discharge power from 1.9 W to 15.0 W decreases the energy efficiency by a factor of 2.88. In this study, the maximum energy efficiency of 47.5 g/kWh is obtained at the lowest discharge power of 1.9 W (Fig. 4b). These results suggest that a balance between the destruction of pollutants and energy efficiency of the plasma-catalytic process should be considered when developing a cost-effective plasma-catalytic technology.



253

254

(a)



255

256

(b)

257 **Fig. 4.** Effect of discharge power on the plasma-catalytic removal of methanol over Mn-  
 258 Ce catalysts: (a) removal efficiency; (b) energy efficiency ( $Q$ : 1 L/min,  $C$ : 3000 ppm).

259

### 260 3.2.2 Effect of Mn percentage

261 Catalyst composition is one of the key factors affecting the plasma-catalytic process of methanol  
 262 removal. The effect of Mn percentage on methanol removal efficiency and energy efficiency at  
 263 different discharge powers has also been investigated, as presented in Fig. 4. Both predicted removal

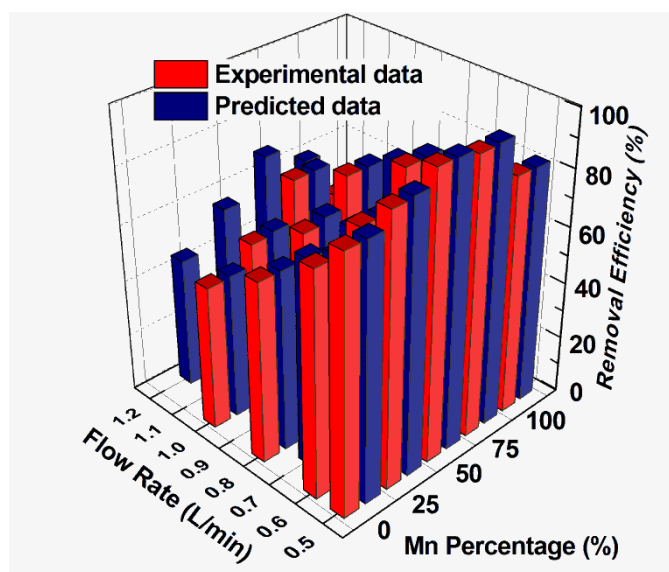
264 efficiency and energy efficiency are in good agreement with the experimental data inside and outside  
265 of the catalyst composition range. In this study, pure  $\text{MnO}_x$  is the least active catalyst for the plasma  
266 removal of methanol followed by pure  $\text{CeO}_2$  in the tested discharge power range. The interaction of  
267 Mn and Ce species significantly enhances the reaction performances and the activity of Mn-Ce  
268 catalysts follow the order of  $\text{Mn}_{50}\text{Ce}_{50} > \text{Mn}_{75}\text{Ce}_{25} > \text{Mn}_{25}\text{Ce}_{75}$ . This agrees with the properties of the  
269 Mn-Ce catalysts given in Table 1 which show that the  $\text{Mn}_{50}\text{Ce}_{50}$  sample has the largest specific  
270 surface area. At the discharge power of 9.4 W, the maximum methanol removal efficiency and energy  
271 efficiency of the system can be achieved at 73.5% and 20.1 g/kWh, respectively, in the presence of  
272 the  $\text{Mn}_{50}\text{Ce}_{50}$  catalyst. Previous work also reported that Mn-Ce oxide catalyst with a molar ratio of  
273 1:1 exhibited the best performance for thermal catalytic oxidation of toluene, ethanol and ethyl acetate  
274 [16]. The influence of Mn content on the energy efficiency of the process follows the similar trend as  
275 the removal efficiency. These results suggest that the catalyst composition significantly affects the  
276 oxidation process in the catalyst bed. Due to the smaller radius of Mn ions ( $\text{Mn}^{2+} = 0.83 \text{ \AA}$ ,  $\text{Mn}^{3+} =$   
277  $0.65 \text{ \AA}$  and  $\text{Ce}^{4+} = 0.97 \text{ \AA}$ ), the partial substitution of  $\text{Ce}^{4+}$  by Mn cations results in the formation of  
278 Mn-Ce solid solutions. Meanwhile,  $\text{Ce}^{3+}$ , oxygen vacancies and unsaturated chemical bonds could be  
279 formed on the catalyst surface to maintain the electroneutrality, which contributes to the formation of  
280 active O species for oxidation reactions [32]. When the Mn content is lower than 50%, Mn particles  
281 are well dispersed on the surface of  $\text{CeO}_2$  and facilitate oxygen mobility in the redox cycles, which  
282 enhances the reducibility of the Mn-Ce catalysts [33]. The oxygen storage capacity is determined by  
283 the redox couple of  $\text{Ce}^{4+}/\text{Ce}^{3+}$ . Further increasing the content of Mn leads to the formation of separated  
284 bulk Mn, and the Mn-O-Mn connections would become more abundant, which may inhibit the  
285 formation of oxygen vacancies on the catalyst surface [34], and in turn decrease the oxidation capacity  
286 of the Mn-rich catalysts (i.e.,  $\text{Mn}_{75}\text{Ce}_{25}$  and pure  $\text{MnO}_x$ ). As a result, both removal efficiency and  
287 energy efficiency are decreased when using the Mn-rich samples.

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290 **3.2.3 Effect of gas flow rate**

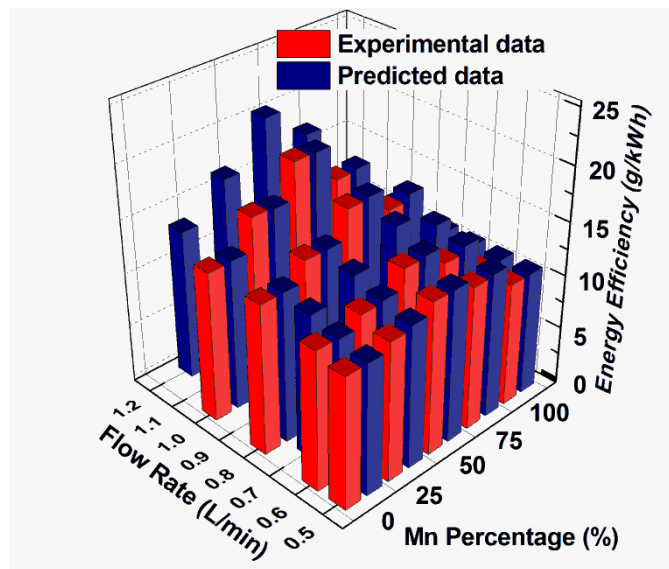
291 Fig. 5 shows the effect of the gas flow rate and Mn-Ce catalyst composition on the removal  
292 efficiency of methanol and energy efficiency of the plasma-catalytic process. There is a perfect match  
293 between the experimental results and predicted data. The removal efficiency of methanol decreases  
294 from 99.5% to 73.3% over the tested flow rate range for the Mn<sub>50</sub>Ce<sub>50</sub> catalyst. The gas flow rate  
295 shows a significant effect on the reaction performance. Increasing the gas flow rate leads to the  
296 decrease of the residence time of pollutants in the plasma region, reducing the possibility of the  
297 collisions between methanol molecules and reactive species, and consequently decreasing the  
298 removal efficiency of methanol. The optimized ANN model predicts the removal efficiency of 89.5%  
299 and 69.3% at the gas flow rate of 0.7 and 1.2 L/min, respectively. However, increasing the flow rate  
300 leads to a significant enhancement in the energy efficiency of the process even though the removal  
301 efficiency is much lower at a high gas flow rate.



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(a)



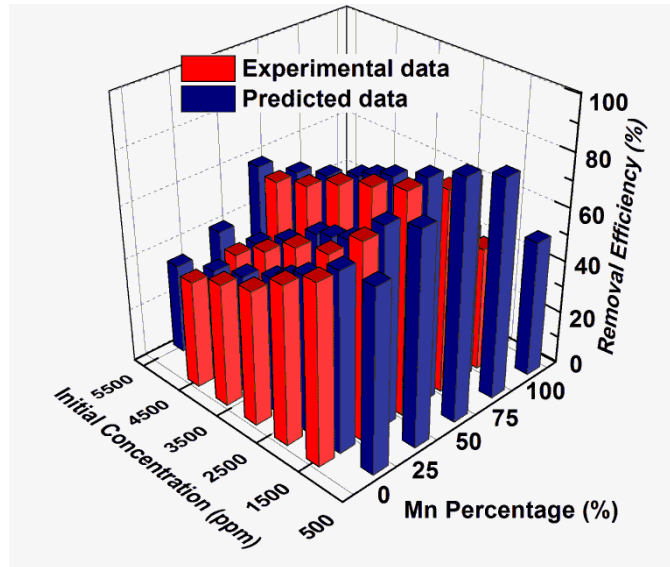
(b)

**Fig. 5.** Effect of gas flow rate on the plasma-catalytic removal of methanol over Mn-Ce catalysts: (a) removal efficiency; (b) energy efficiency ( $P$ : 9.4 W,  $C$ : 3000 ppm).

### 3.2.4 Effect of initial concentration of methanol

The influence of the initial methanol concentration on the plasma-catalytic removal of methanol over different Mn-Ce catalysts is shown in Fig. 6a. The experimental results are well matched by the ANN simulation. It is clear that the removal efficiency of methanol increases with decreasing initial methanol concentration in the gas flow regardless of the catalysts used. For the  $Mn_{50}Ce_{50}$  catalyst, the experimental removal efficiency decreases from 82.7% to 63.3% when the initial concentration of methanol increases from 1500 ppm to 4500 ppm. For a given plasma-catalytic system, the number density of plasma-generated reactive species and active sites could be similar at a same working condition. At this point, only limited number of reactive species and active sites are available for the oxidation of methanol molecules at higher initial concentration, which subsequently reduces the removal efficiency. In contrast, the energy efficiency of the plasma-catalytic process changes from 11.3 g/kWh to 26.0 g/kWh as the concentration of methanol rises from 1500 ppm to 4500 ppm (Fig. 6b). Note that the energy efficiency at 4500 ppm is only 2.3 times of that at 1500 ppm, which is in

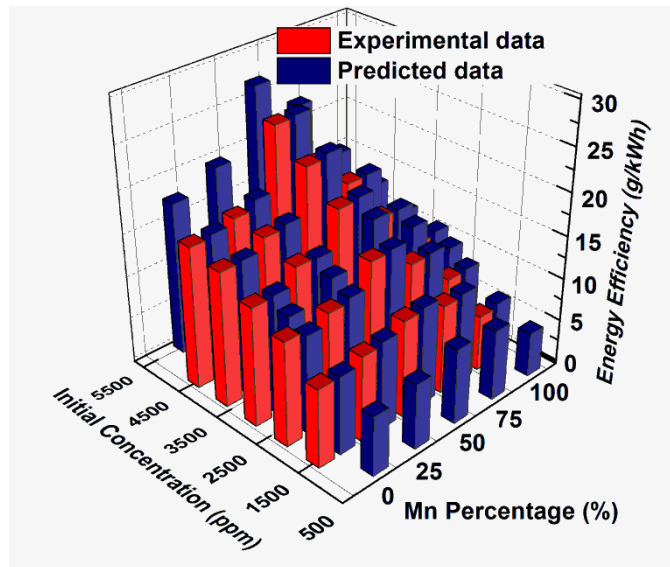
323 line with the results of reduced removal efficiency at high initial concentration. The ANN model  
324 predicts that the energy efficiency of the process increases to 27.3 g/kWh at an initial concentration  
325 of methanol of 5500 ppm.



326

327

(a)



328

329

330

(b)

331 **Fig. 6.** Effect of initial concentration of methanol on the plasma-catalytic process: (a)

332 removal efficiency; (b) energy efficiency ( $P$ : 9.4 W,  $Q$ : 1 L/min).

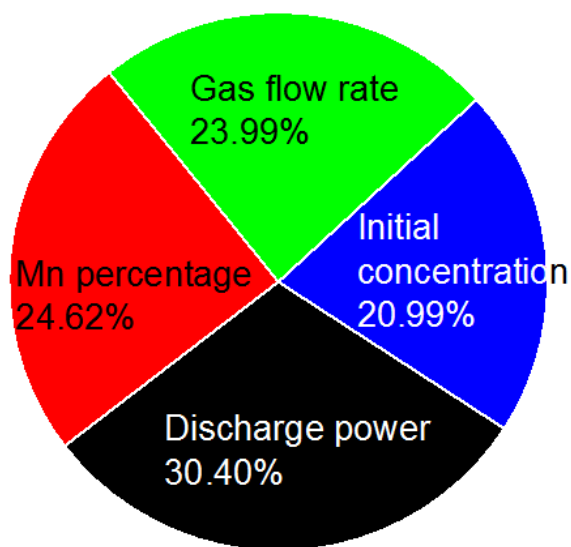
333

334 **3.3 Contribution of different process parameters**



335 Net weight matrix and Garson equation were used in this work to evaluate the relative importance  
336 of each process parameter on the plasma chemical reactions [35]. The weight matrix produced by the  
337 well-trained ANN model is listed in Table S2 in the Supporting Information, while the calculated  
338 relative importance of each process parameter is plotted in Fig. 7. Both gas flow rate and catalyst  
339 composition (Mn percentage) show a significant impact on the removal efficiency of methanol with  
340 a relative weight of ~31%, while the initial concentration of methanol plays a very weak role in the  
341 plasma-catalytic abatement of methanol, which suggests that the plasma system is suitable for the  
342 removal of methanol with a wide range of concentration. The discharge power is found to be the most  
343 important factor affecting the energy efficiency of the process, while the relative importance of other  
344 process parameters on the energy efficiency is similar, ranging from 20.99% to 24.62%.

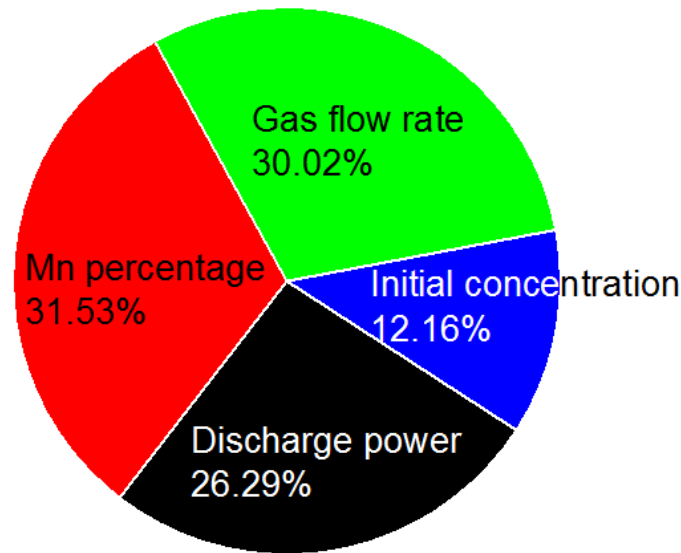
345



346

347

(a)



(b)

348

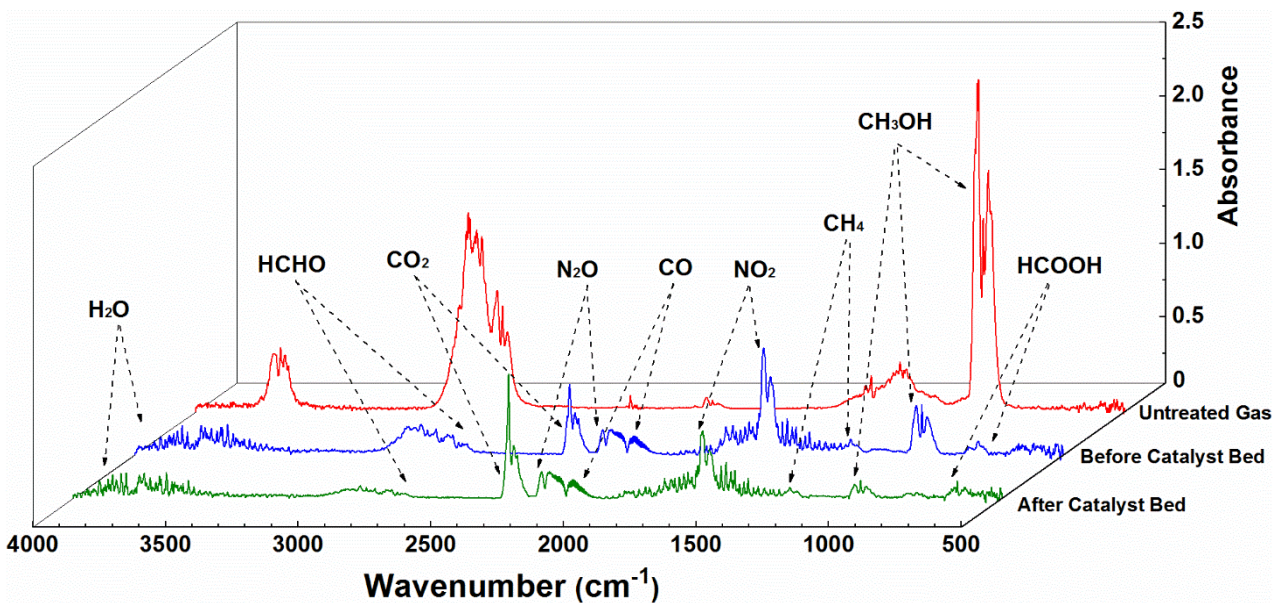
349

350 **Fig. 7.** Relative importance (%) of processing parameters on plasma-catalytic removal of methanol:

351 (a) removal efficiency; (b) energy efficiency.

352

353 **3.4 Reaction mechanisms and pathways**



354

355 **Fig. 8.** FTIR spectra of plasma-catalytic removal of methanol over  $Mn_{50}Ce_{50}$  catalyst ( $P$ : 15.0 W,  $Q$ :

356 1 L/min,  $C$ : 3000 ppm).

357

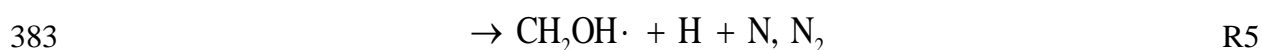
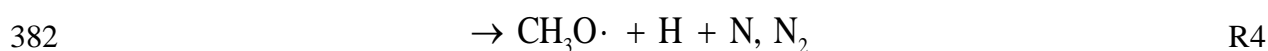
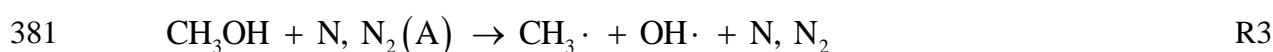
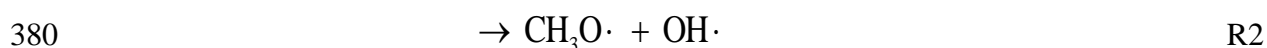
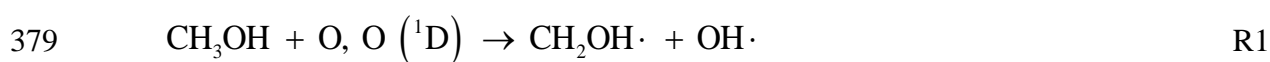
358 Fig. 8 shows the distribution of the gas products in the plasma-catalytic removal of methanol

359 over the  $Mn_{50}Ce_{50}$  catalyst. The main gas products sampled before the catalyst bed were CO, CO<sub>2</sub>

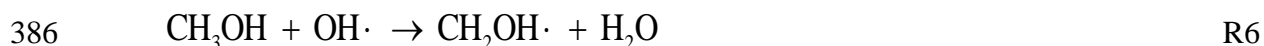
360 and H<sub>2</sub>O, while small amount of CH<sub>4</sub>, HCHO, HCOOH, N<sub>2</sub>O and NO<sub>2</sub> were also detected. Ozone was  
 361 not detected since it could be consumed in the oxidation reactions or decomposed by the local heating  
 362 in the plasma. Similar gas products were detected at the outlet of the plasma reactor after the catalyst  
 363 bed. However, the intensity of most gas products (CO, CH<sub>4</sub>, HCHO, HCOOH, N<sub>2</sub>O and NO<sub>2</sub>) is  
 364 significantly decreased except CO<sub>2</sub> and H<sub>2</sub>O at the exit of the DBD reactor. These results suggest that  
 365 the catalyst bed placed after the plasma region plays an important role in the further oxidation of  
 366 methanol and by-products in this post-plasma catalysis system.

367 In this post-plasma catalysis system, the catalyst bed is located at 5 cm downstream of the plasma  
 368 region. Only long-lived species (e.g. methanol and intermediates) can reach the surface of the Mn-Ce  
 369 catalysts, while most short-lived species such as O and OH could be quenched before reaching the  
 370 catalyst surface due to their extremely short lifetime and high chemical activity. Thus, the dominant  
 371 reaction pathways of methanol removal in the two-stage post-plasma catalytic process without extra  
 372 heating can be identified as two separate steps: plasma reaction in the discharge region and catalytic  
 373 reaction in the catalyst bed, as shown in Fig. 8.

374 It is well known that abatement of dilute VOCs in air plasmas is initiated by direct electron impact  
 375 dissociation of carrier gas (nitrogen and oxygen) to form chemically reactive species such as O, O  
 376 (<sup>1</sup>D), N and N<sub>2</sub> (A) for the stepwise decomposition and oxidation of pollutants and/or intermediates  
 377 into CO, CO<sub>2</sub>, H<sub>2</sub>O and other by-products. The formation of these reactive species allows methanol  
 378 decomposition or oxidation through the following reactions (R1-R5) [36]:



384 Hydroxyl radicals (OH·) generated from R1, R2 and R3 can also oxidize methanol molecules via  
385 [37]:



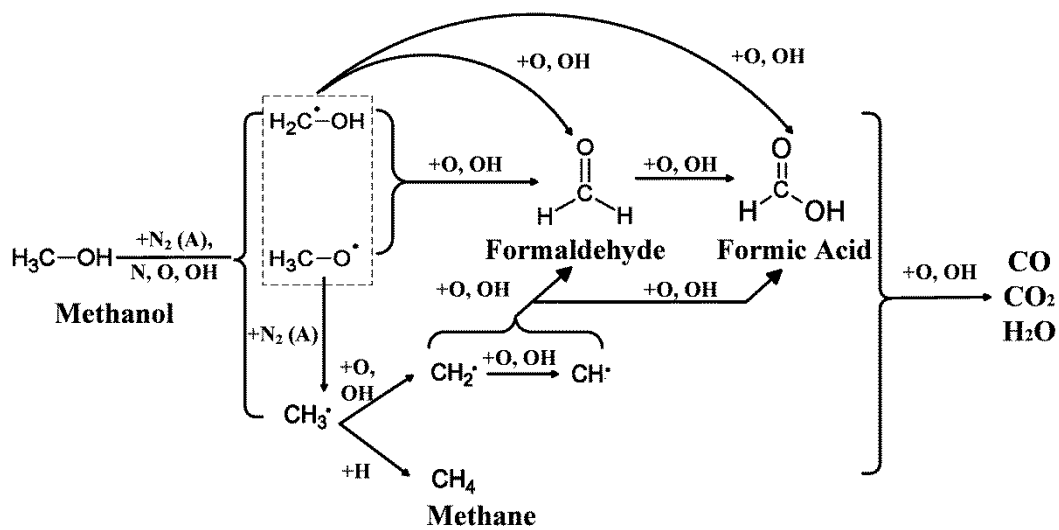
388 Hamdane et al. reported that the reaction between OH· and CH<sub>3</sub>OH is a major pathway for  
389 methanol oxidation [37]. However, the effect of electron impact dissociation could be weak or  
390 negligible for the dissociation of methanol and other by-products due to the relatively low  
391 concentration of these products compared to carrier gas.

392 CH<sub>3</sub>·, CH<sub>2</sub>OH· and CH<sub>3</sub>O· radicals are the main intermediates of methanol decomposition and  
393 oxidation in the air DBD. Previous works also reported that CH<sub>2</sub>OH· and CH<sub>3</sub>O· are very important  
394 radicals for the oxidation of higher hydrocarbons and oxygenates [38]. H-abstractions of CH<sub>2</sub>OH· and  
395 CH<sub>3</sub>O· radicals are also likely to occur via reactions with O, H and OH·, forming CH<sub>2</sub>O and HCO·.  
396 In the air plasma removal of methanol, CH<sub>3</sub>· radicals can be reacted with O and OH to form CH<sub>2</sub>·  
397 radicals, while some of the CH<sub>3</sub>· radicals recombine with H atoms to form CH<sub>4</sub> (Fig. 8). In the  
398 presence of oxidative radicals, CH<sub>2</sub>· radicals can also be converted to CH<sub>2</sub>O and HCO·. Both CH<sub>2</sub>O  
399 and HCO· can react with O and OH radicals, and form HCOOH [39]. The intermediates and by-  
400 products could be further oxidized to form end-products such as CO, CO<sub>2</sub> and H<sub>2</sub>O.

401 In the catalyst bed, methanol and by-products in the gas mixture were adsorbed onto the surface  
402 active sites prior to catalytic reactions. It is generally recognized that the oxidation of VOCs on Mn  
403 catalysts proceeds via the classical Mars-van Krevelen (MVK) mechanism [40][41]. According to  
404 this mechanism, adsorbed VOC molecules were oxidized by active surface oxygen species, while the  
405 resultant oxygen vacancies could be replenished by gas phase oxygen. The alternative oxidation and  
406 reduction of metal active sites on the catalyst surface in the whole catalytic reaction makes the supply  
407 of oxygen species as a rate-determining step [42]. CeO<sub>2</sub> acted as a reservoir for the release and storage  
408 of oxygen as a result of the Ce<sup>4+</sup>/Ce<sup>3+</sup> redox cycle in the Mn-Ce oxide catalysts. The interactions  
409 between Mn and Ce oxides in the Mn-Ce catalysts shows a synergistic effect in oxygen activation,

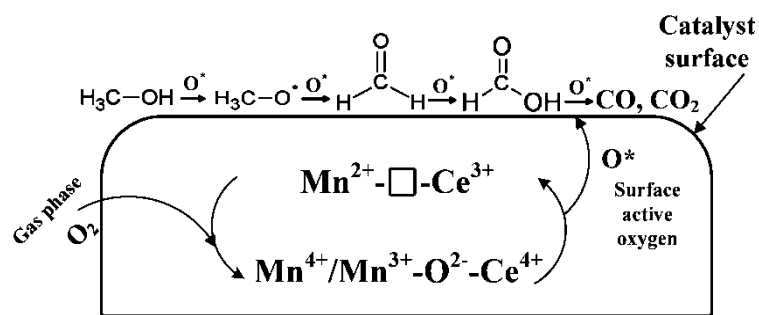
410 which enhances the oxygen mobility on the catalysts and accelerates the conversion of oxygen from  
 411 chemisorbed and lattice oxygen to active oxygen species ( $O^*$ ) on the oxygen vacancies and active  
 412 metal sites. These processes lead to the deep oxidation of methanol and intermediates by surface  
 413 active oxygen in the catalyst bed [43]. Finocchio et al. reported that methanol adsorbed onto the  
 414 surface of Mn-based catalysts can be dissociated and resulted in the break of O-H bonds [44]. The  
 415 formed  $CH_3O\cdot$  can be further dissociated to HCHO and H with the aid of  $O^*$  [45]. The conversion of  
 416 HCHO to HCOOH via  $HCO\cdot$  on the surface of Mn catalysts was also reported [46]. A fraction of  
 417 these intermediates and by-products can be further oxidized by  $O^*$  and finally desorbed as CO and  
 418  $CO_2$ . The inhibition of  $NO_x$  formation in a post-plasma catalysis system are mainly attributed to the  
 419 oxidation of  $NO_x$  to  $HNO_x$  and surface adsorbed  $NO_2^-$  or  $NO_3^-$  cations [10].

420



421

422



423

424

425 **Fig. 9.** Plausible major reaction pathways of methanol removal in the post-plasma catalysis system:  
426 (a) Plasma induced chemical reactions in the discharge region; (b) Catalytic reactions on the  
427 catalyst surface. The 'square' symbol represents oxygen vacancies on the surface of the Mn-Ce  
428 catalysts.

429

430

#### 431 **4. Conclusions**

432 In this study, effective removal of methanol over Mn-Ce oxide catalysts with different Mn/Ce  
433 molar ratios has been achieved in a post-plasma catalysis system. Compared to pure  $\text{MnO}_x$  and  $\text{CeO}_2$   
434 oxide catalysts, the combination of plasma and binary Mn-Ce catalysts significantly enhances both  
435 methanol removal efficiency and energy efficiency of the plasma-catalytic process, while the  
436  $\text{Mn}_{50}\text{Ce}_{50}$  catalysts exhibits the best performance among all the tested catalysts. The presence of these  
437 Mn-Ce catalysts in the plasma process also inhibits the formation of various by-products including  
438  $\text{CH}_4$ ,  $\text{HCHO}$  and  $\text{HCOOH}$ . Possible reaction pathways have been proposed based on the detected by-  
439 products. A well-trained and optimized three layer neural network has been used to get a better  
440 understanding of the effect and importance of different processing parameters and catalyst  
441 composition on the plasma chemical reaction. Sensitivity analysis shows that catalyst composition  
442 (Mn percentage) is the most important factor affecting the removal efficiency of methanol, while the  
443 discharge power plays a crucial role in the energy efficiency of the plasma-catalytic process. The  
444 good agreements between experimental and predicted results indicate ANN model can be an effective  
445 approach for fast and reliable simulation and prediction of the complex plasma-catalytic process.

446

#### 447 **Supporting Information**

448 Definition of MSE and SDE; Comparison of 5 best combinations of BP algorithms and transfer  
449 functions with a hidden layer of 5 neurons (Table S1); MSE as a function of neuron number for the  
450 LM-TT configuration (Fig. S1); Comparison between measured removal efficiency T and predicted

451 data Y (Fig. S2); Weight matrices W1 (weights between the input and hidden layers) and W2 (weights  
452 between the hidden and output layer) (Table S2).

453

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458

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