



Remarkable selectivity of polyvinyl alcohol oxidation: An insight from ambient air plasma in the presence and absence of TiO₂

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ABSTRACT

Initiating depolymerization at ambient temperature by nonthermal air plasma provides a novel and promising route to convert polymer wastes to valuable small molecules. This study showed that the selectivity of partial oxidation of polyvinyl alcohol (PVA) initiated by nonthermal air plasma can be controlled by the polymer to TiO₂ ratio and AC (alternative current) voltage and frequency. Transient responses to applying AC (alternating current) power showed that the CO₂ led to the formation of CO, propionaldehyde, and acetaldehyde. Significant formation of propionaldehyde showed that -C-OH in PVA can be directly converted to CH₃ in propionaldehyde, unraveling a new reaction pathway in nonthermal plasma chemistry. The selectivity of aldehydes is at the same level as that of CO₂. The selectivity of aldehydes was further enhanced by nitrogen plasma while the selectivity toward CO₂ was increased in the presence of TiO₂. This study demonstrated that ambient nonthermal air plasma could provide a potentially effective approach for the selective conversion of polymers to desired small molecules.

1. Introduction

Recycling of polymer waste into valuable compounds is highly challenging because of their complexity in compositions and structures [1–3]. To tackle this challenge, we simplified polymers to a group of chemical bonds: C–C, C–H, C–O, O–H, C–N, and C=C, which are in many widely used polymers. In this study, we selected polyvinyl alcohol (PVA) as a model compound for testing the activity of nonthermal air plasma for the scission of these chemical bonds because PVA contains 4 different chemical bonds: C–H, C–C, C–O, and O–H. Although PVA is not a commodity polymer that is used in large quantities in the polymer industry, it is known for its excellent film-forming, emulsifying, and adhesive properties and has found many niche applications. PVA can be found as one of the components in many widely used polymeric materials.

Oxygen and nitrogen radicals/ions (charged particles) and electrons in nonthermal air plasma could serve as a low-cost reactant and initiator, respectively for partial oxidation of PVA, leading to the breaking of the C–C bond in PVA, producing value-added small molecules. The

possibility of operating nonthermal air plasma in ambient conditions, i.e., 25 °C and 1 atm, could eliminate the problems of coking and tar formations as well as low selectivity, commonly observed in thermal catalysis and pyrolysis. In addition, nonthermal plasma can be produced with high energy efficiency through dielectric barrier discharge. Electrons in nonthermal plasma have a significantly higher temperature (10⁴–10⁵ K), than those of charged particles. Dielectric Barrier Discharge (DBD) plasma often maintains its particle temperatures near ambient temperatures which can be interpreted as having a low thermal energy content. The lower thermal energy of charged particles allows nonthermal plasma to be produced with less energy compared to thermal plasma which is characterized by equal temperatures of electrons and charged particles at temperatures above at least 4000 °C. The significantly high thermal energy of charged particles in thermal plasma does not provide energy-efficient bond-breaking processes [4,5].

We attempted to use nonthermal hydrogen plasma for catalytic hydrogenolysis of polystyrene and polyethylene. High selectivity toward gaseous C₁ – C₃ hydrocarbon was achieved at temperatures below 100 °C [6–8]. We also tested Ar and CO₂ nonthermal plasma for cracking

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of rubber to ethane and ethylene on a Ni catalyst [8]. These studies substantiate the feasibility of selective scission of C–C bonds in polymers by nonthermal plasma of H₂, Ar, and CO₂ at low temperatures. However, the use of hydrogen as a reactant does raise concern about its explosion hazard. Uneven distribution of an electric field could produce a spark that denotes a rapid combustion (explosion) of hydrogen with oxygen. The use of Ar and CO₂ raises a cost issue.

Nonthermal air plasma used in this study and hydrogen, Ar, as well as CO₂ plasma used in previous studies were produced by dielectric barrier discharge with AC electric power [9–12]. In general, high AC voltage and frequency produce a high concentration of nonthermal plasma which is produced in the vicinity of the surface of the quartz reactor which serves as a dielectric barrier. It should be noted that the generation of dielectric discharge occurs at the same time as the dielectric heating of a quartz reactor. Thus, in this study, we specifically limited the time of applying electric power to <6 s to avoid raising the reactor temperature above 65 °C due to dielectric heating.

TiO₂ was selected for this study because it plays a significant role in both thermal and photo-catalytic oxidation of hydrocarbons [13,14]. Titanium dioxide (TiO₂) can produce oxygen vacancies which are known for their total and partial oxidation activities through heating in reducing environment or under UV-irradiation. Several studies have shown oxygen vacancies can also be produced by nonthermal oxygen and hydrogen plasma [15].

This study reports results of a surprisingly selective partial oxidation of PVA in nonthermal air plasma at ambient conditions. Both nitrogen and oxygen in air plasma can selectively break C–C bonds and O–H bonds in PVA, producing acetaldehyde and propionaldehyde. The presence of TiO₂ catalysts enhanced the total oxidation of PVA to CO₂. The sequence of product formation observed from transient responses to applying a pulse of AC power suggests that CO₂ and aldehydes were produced from two independent pathways. The results shown in Figs. 2 (c) and (f) as well as Figs. 3 (c) and (f) suggest that the CO₂ formation pathway could be suppressed without significantly inhibiting the aldehyde formation pathway. The direct formation of propionaldehyde (CH₃CH₂CHO) from PVA (–CH₂–CHOH–) unraveled a new nonthermal plasma reaction pathway for converting alcohol functional group (CHOH) in PVA to CH₃ in propionaldehyde.

2. Experimental

Materials. Poly(vinyl alcohol) (PVA, Mw = 95,000 g/mol, Acros Organics – average size 400 μm), Titanium(IV) oxide (Anatase, Sigma-Aldrich, <25 nm particle size), were used as received.

The experiments were conducted using a nonthermal Dielectric Barrier Discharge (DBD) plasma reactor, which was reported previously and shown in Fig. S1 in supplemental information. The reactor's core component was a cylindrical quartz tube, measuring 13 mm in outer diameter and 11.5 mm in inner diameter, chosen for its dielectric property, durability, and resistance to temperature variation and chemical corrosion. The discharge area within the reactor, where plasma interactions and reactions occurred, was approximately 50 mm in length, a dimension critical to maintaining consistent plasma characteristics throughout the experiments. Central to the functioning of the DBD reactor was its electrode configuration. The reactor utilized a dual-electrode system. The ground electrode was a copper rod, 40 mm in diameter and 100 mm in length, positioned along the central axis of the quartz tube. Surrounding the exterior of the quartz tube was the high voltage electrode, made of copper tape. This electrode was wrapped uniformly around the tube, ensuring an even distribution of the electric field, and thereby facilitating uniform plasma generation along the entire length of the discharge zone.

For each experiment, the reactor was prepared by introducing 1 g of PVA powder into the discharge space between the electrodes. This PVA powder, with a particle size of approximately 400 μm, was chosen for its standard chemical composition and consistency in quality. Such

uniformity in the reactant material was essential for ensuring reproducibility. Mixtures of PVA_TiO₂ (4:1) and PVA_TiO₂ (2:1) molar ratios were also tested.

The generation and regulation of the non-thermal plasma within the DBD reactor were achieved using a PVM500–2500 plasma generator. This generator could produce a range of voltages from 6 kV to 10.5 kV and could operate at frequencies between 20 and 70 kHz, parameters that were vital for tailoring the plasma characteristics to the specific requirements of each experiment. Operating conditions were carefully controlled to replicate typical atmospheric pressure environments, with a stable ambient temperature of approximately 25 °C as the initial reaction temperature. Air, nitrogen, or pure CO₂ gas was fed into the reactor at a flow rate of 33 cm³/min. The quantities of CO₂ and propionaldehyde produced were determined by a calibration procedure which involve injecting a known quantity of the specie to be calibrated to the reactor in the absence of reaction and then monitoring the IR absorbance profile as show in Fig. S8 and S9. Both acetaldehyde and propionaldehyde have a similar dipole moment and extinction coefficient. Thus, we did not further calibrate the quantity of acetaldehyde.

A significant aspect of this experimental study was the transient kinetic analysis. This analysis involved introducing specific perturbations to the reaction system, such as a pulse change in the applied AC voltage where AC voltage was raised from 0 to a specific voltage for <6 s and then switched back to zero. This perturbation was designed to initiate the reaction for a short period of time and the terminate the nonthermal plasma to minimize raising the temperature of reactor and polymer samples. Rising temperature is a manifestation of thermal energy loss – an indication of low efficiency operation. The responses of the products to this perturbation were continuously and meticulously monitored using an infrared spectrometer with a DRIFT cell where a stainless-steel plate was placed on the base of the DRIFT to reflect the IR back to the DRIFT accessory. The details of this cell arrangement were previously reported. This instrument was not only crucial for real-time monitoring of the reactions but also provided detailed estimations and determinations of the effluent compositions exiting the reactor. The infrared (IR) intensities of gaseous products were plotted as a function of time. Comparison of IR intensity vs time profiles for specific products allowed us to decipher the complex interplay of operating variables within the reaction environment and understand the underlying mechanisms governing the plasma-assisted reactions.

3. Results and discussion

Fig. 1 shows the IR spectra of gaseous products as a function of time taken during turning on AC electric field for 5.43 s. The major IR-observable products were CO₂, CO, propionaldehyde (CH₃CH₂CHO), and acetaldehyde (CH₃CHO). The minor products were methane and formaldehyde. The IR intensities of major products versus time profiles were plotted in Fig. 2 with an adjustment of the time at which the IR-observable products emerged to 0 s. Turning on AC electric field led to a sharp increase in CO₂ and then followed by CO, propionaldehyde, and acetaldehyde, indicating occurrence of total oxidation of PVA to CO₂ and partial oxidation of PVA to aldehydes. Since CO formation lagged CO₂ formation, CO must could be a secondary product that is produced from CO₂. On the other word, if CO is a primary product, its formation should lead that of CO₂. Turning off AC power led to a rapid decline in CO₂ and CO formation, further supporting the proposition that CO is a secondary product.

It is crucial to point out that the nonthermal plasma reactor is operated in a semi-batch mode where nonthermal plasma were produced and flowed through the polymer and catalyst bed. 5.43 s of AC power produced the IR intensities (i.e., products) vs time profiles last for about 250 s. This is because of the dispersion of the reactor tube and the connection tubes to the IR cell. The CO₂ profile can serve as an index of the air plasma intensity in the reactor since CO₂ was the primary product and led the formation of other products and has the least effect on its

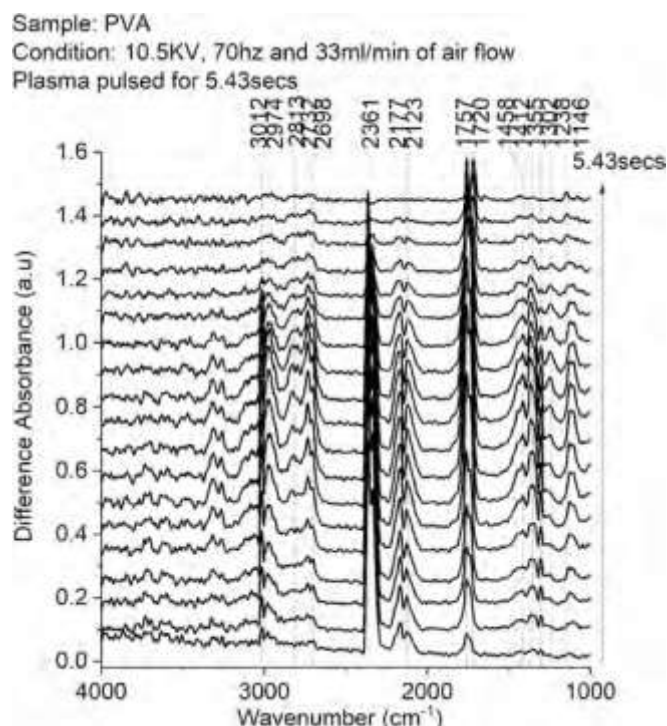


Fig. 1. Difference Absorbance spectra of Non-thermal Plasma on pure PVA under air at a flow rate of 33 ml/min at 25 °C.

flow by diffusion and re-adsorption compared with other products.

Figs. 2 also showed that the formation of aldehydes lagged that of CO₂. Both acetaldehyde and propionaldehyde emerged at the same time for pure PVA (blank run in the absence of TiO₂) in Fig. 2(a) while propionaldehyde rose at a faster rate than acetaldehyde. Their emergence at the same time suggests they may be formed simultaneously upon occurrence of C–C bond scission. The amount of propionaldehyde produced is about the same as that of acetaldehyde, further suggesting that both are primary products which are formed at the same time scale. Increase the ratio of TiO₂ to PVA led to a significant decrease in acetaldehyde, indicating that TiO₂ is more active for oxidizing acetaldehyde than propionaldehyde. We will further elaborate these steps in Scheme 1. Trailing response of acetaldehyde could be due to its high dipole moment of C–O which allow it to form a stronger hydrogen bonding with not yet reacted -C–OH in PVA. Such a proposition can be supported by a high solubility of acetaldehyde in water compared to that of propionaldehyde.

Scheme 1 illustrates the key steps involved in the formation of these products. The observation of high selectivity toward aldehyde products suggests a high fraction of C–O bond in alcohol functional group (-C–OH) of PVA was preserved and the alcohol functional groups were oxidatively dehydrogenated to -C=O by oxygen and nitrogen plasma. We suggest that C₀–O in Scheme 1 was oxidized to CO₂ through abstraction of H of its neighboring C–H, leading to generation of free radical in the carbon backbone of PVA, which then subsequently led to the breaking C–C bonding between C of C–O and C of CH. The hydrogen abstraction from -C–OH and C–H by oxygen radical or charged species is expected to occur on those extruded -C–OH which are exposed to oxygen and nitrogen plasma.

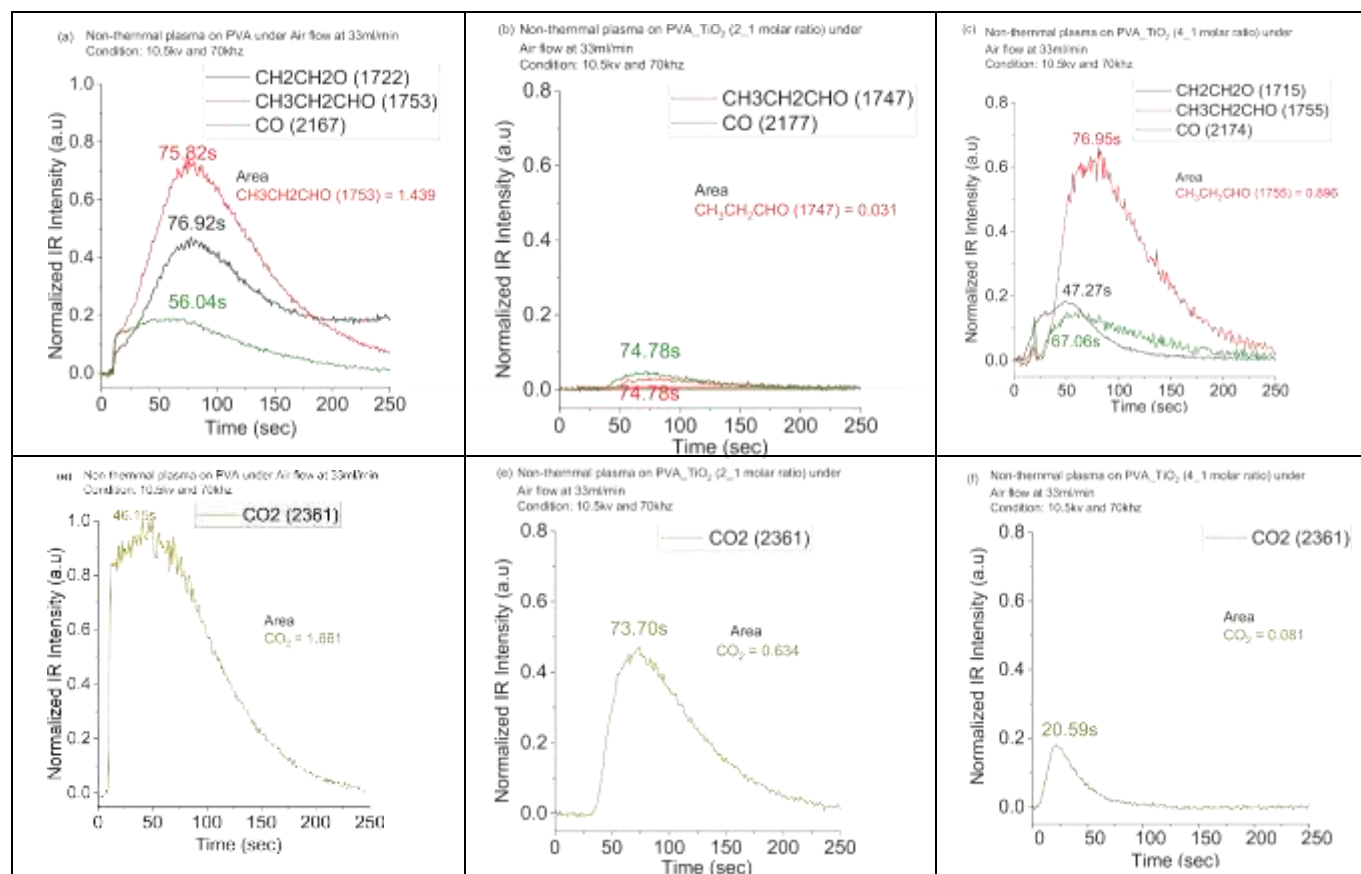
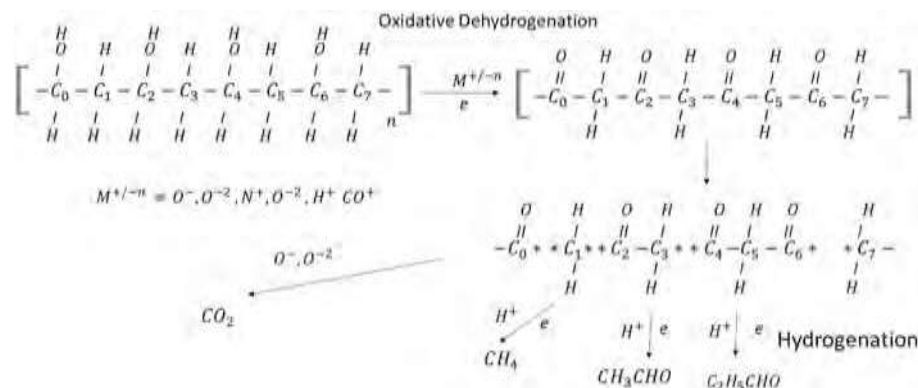


Fig. 2. IR Intensity profiles show the lead vs lag relationship of products formed during non-thermal plasma pulse for 3 s under air flow at 10.5 kv and 70 kHz for aldehydes in (a) pure PVA, (b) 2:1 PVA_TiO₂ molar ratio and (c) 4:1 PVA_TiO₂ molar ratio mixtures and CO₂ in (d) pure PVA (e) 2:1 PVA_TiO₂ molar ratio and (f) 4:1 PVA_TiO₂ molar ratio mixtures at 25 °C. The areas under propionaldehyde and CO₂ can be converted to the quantity (μmol) with the procedures and calibration results in Fig. S8–1/ 2 and Fig. S9–1/ 2. The rates of CO₂ and propionaldehyde formation are listed in Table S6.



Scheme 1. Proposed reaction pathway of rubber with nonthermal plasma * represents a charged species or free radical.

The radicals in the carbon backbone of PVA produced from C–C bond scission are expected to lead to breaking C–C bond to scission of the C–C bond. The breaking of C1–C2 bond and C4–C5 bond would lead to the formation of acetone. However, acetone was not observed as one of the gaseous products. It is worth noting that both aldehyde and ketone give the C=O bond in the same region of 1710–1750 cm^{-1} , but ketone such as acetone also give two strong C–H deformation band in 1350–1440 cm^{-1} which was absent in this study. Thus, C–C scission must occur at C1–C2 and C3–C4 to produce acetaldehyde as well as C3–C4 and C6–C7 to produce propionaldehyde. Furthermore, one of C–O in C4 and C7 must be hydrogenated to CH_3 . This step is expected to take place in a reducing environment which could be produced after oxygen radical and charged species were consumed. The source of hydrogen is probably H from H_2O or -CH or OH of neighboring PVA. In organic chemistry and catalytic chemistry [16–20], hydrogenation of C–O functional group and conversion of C–OH functional to CH_3 involve several tedious process steps. This is the first time such conversion reactions can be achieved by a single process step, showing unique chemistry in nonthermal air plasma. We will further verify this step by adding D_2O to the reaction system.

Note that bond-breaking and -formation take place at a time scale of less than pico-second. Our IR observation of product evolution occurred at a time scale of second, indicating diffusion and reabsorption control the rate for these gaseous products to reach the reactor exit. Both aldehyde molecules are significantly larger than CO_2 and CO so that they would diffuse at a slower rate than CO_2/CO . Their polar C–O allowed them to re-adsorb on those not-yet reacted -C–OH through hydrogen bonding, further increasing their travel time to the reactor exit.

The reaction scheme 1 can be further extended to interpret results obtained in the presence of TiO_2 . The ratio of PVA to TiO_2 of 2:1 led to nearly complete oxidation of PVA to CO_2 . Decreasing the amount of TiO_2 (PVA: TiO_2 = 4:1 M ratio) led to the return of aldehyde products and CO. The fact that CO_2 was produced at about the same level while less TiO_2 gives more CO in Fig. 2(c) indicates that CO is not a secondary product produced from CO_2 . CO is a primary product which was produced by which C–C bond scission occurs. We can conclude that the observed lead-lag relation among these IR-observable products is not related to the sequence of bond-breaking and bond formation but relevant to their diffusion and re-adsorption.

Comparison of product profiles in Figs. 2 further unraveled an unexpected finding that CO_2 profile is the smallest and last with a shortest period while their aldehyde product profiles are at the same level of those without TiO_2 catalyst, suggesting that the rate and selectivity of a partial oxidation of PVA to aldehyde can be finely tuned by the polymer to catalyst ratio. We can assume that the CO_2 profile represents the intensity profile of air plasma in the reactor since CO_2 is the most direct oxidation product of which evolution profile is least affected by re-adsorption and diffusion of molecules in the flow.

The observation of a prominent propionaldehyde profile which

significantly lagged a small CO_2 profile in Fig. 2 (c) is a significant new finding that total oxidation of PVA to CO_2 and partial oxidation of PVA to aldehyde does not occur at the same time. Partial oxidation continued to occur as the total oxidation product, CO_2 , left the reaction zone, giving a prominent propionaldehyde profile 78.9 s compared with a small CO_2 profile at 20.5 s. We can conclude that the concentration of TiO_2 in the reaction zone greatly influences the activity of air plasma on total oxidation and partial oxidation. We can also postulate that (i) CO_2 is produced from PVA in the vicinity of TiO_2 catalyst particle while aldehyde is produced from those PVA far from TiO_2 particles (ii) Those air plasma far from TiO_2 particles have a proper partial oxidative activity. These postulations deserve further investigation.

To unravel the role of nitrogen played in air plasma, we further studied nonthermal nitrogen-assisted reaction by replacing air with nitrogen. The results in Figs. 3(a), (b) and (c) show that the same products were evolved with the same sequence. Because of the absence of oxygen, the selectivity toward CO_2 is largely suppressed as compared with other products, further showing that CO_2 is formed by an independent pathway where the source of oxygen could be from water or oxygen in TiO_2 . We plan to further study this pathway by further depleting the availability of oxygen and evaluate the possibility for further enhancing aldehyde selectivity. The observed formation of less amount of CO_2 in the presence of TiO_2 is because less amount of PVA was in the nonthermal plasma zone.

The IR intensities vs time profiles provide the lead-lag relation of product evolution. The area under the IR vs time curve represents the amount of the product produced. The trailing responses produced from air plasma in Fig. 2 gave a significantly larger area (i.e., amount of product) than those from nitrogen plasma in Fig. 3. Oxygen plasma is consumed through reaction and the recombination of charged particles and electrons immediately upon turning off AC power. These trailing responses showed lasting effect of oxygen plasma on the product formation and suggested that reactive oxygen species (ROS) trapped in the polymer pores continue to perform partial oxidation for many seconds. It is obvious that the ratio of O_2 to nitrogen is an important parameter to control the concentration at ROS.

One key issue is if this nonthermal plasma approach can give a sufficient rate for product formation. We defined the rates for the formation of propionaldehyde as the quantity, μmol of propionaldehyde produced per gram of polymer per sec ($\mu\text{mol/g sec}$) which are listed in Table S6 and S7. The rate for propionaldehyde formation is in the 0.05–2.4 range for nonthermal air plasma and in the 0.1–0.7 range for nonthermal nitrogen plasma. The rate of CO_2 formation is one order of magnitude higher than that of propionaldehyde. It is worth noting that the rate of many heterogeneous catalytic reaction is in the order of 1–10 ($\mu\text{mol/g sec}$) [21,22]. Although the rate for our nonthermal reaction using the weight of solid polymer as a basis in contrast to catalytic reaction using the weight of catalyst as a basis, the rate of propionaldehyde formation falls in a similar range as catalytic reaction. The similarity in the rates

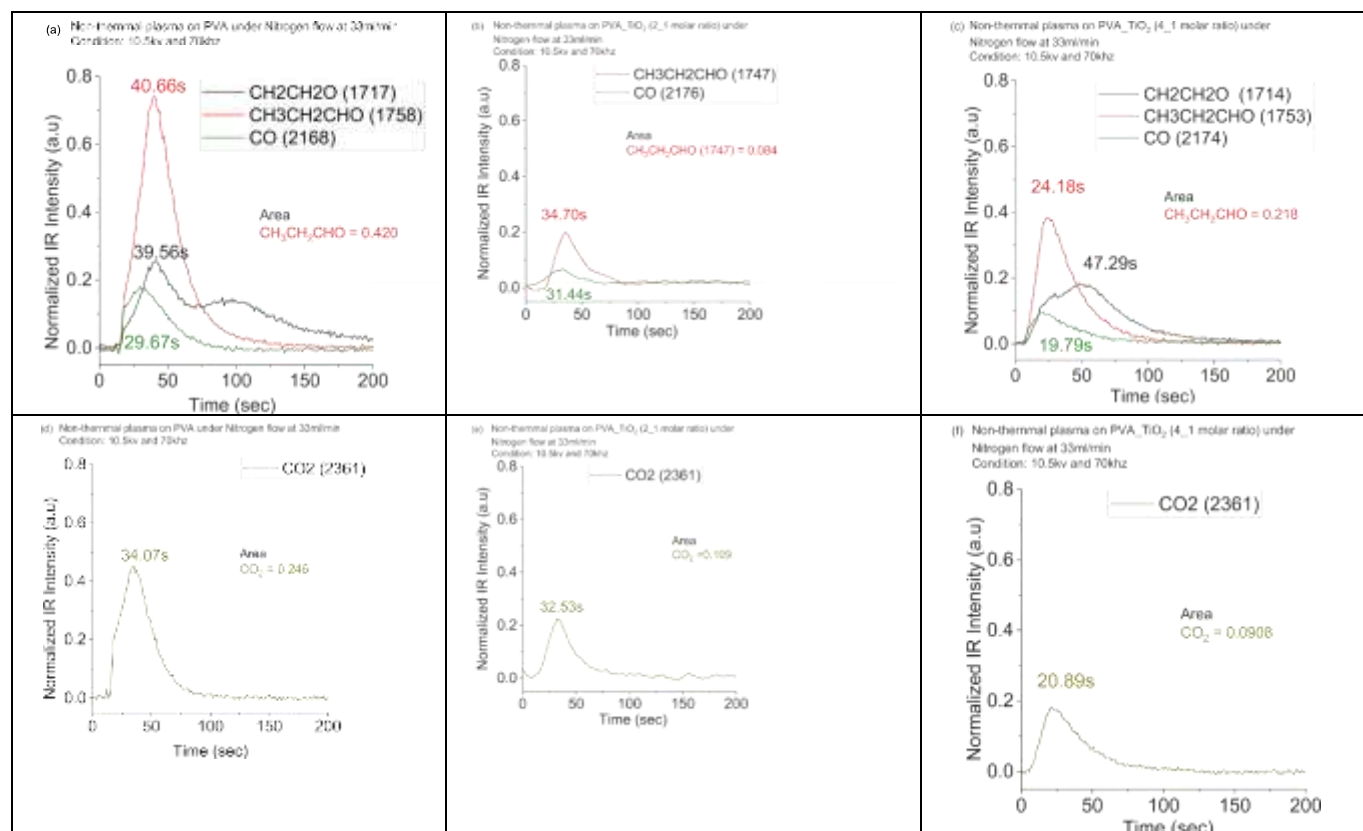


Fig. 3. IR Intensity profiles showing the lead vs lag relationship of products formed during non-thermal plasma pulse for 3 s under Nitrogen flow at 10.5 kv and 70 kHz for aldehydes in (a) pure PVA, (blank run in the absence of TiO₂) (b) 2:1 PVA_TiO₂ molar ratio and (c) 4:1 PVA_TiO₂ molar ratio mixtures and CO₂ in (d) pure PVA (e) 2:1 PVA_TiO₂ molar ratio and (f) 4:1 PVA_TiO₂ molar ratio mixtures at 25 °C. The rates of CO₂ and propionaldehyde formation are listed in Table S7.

unrevealed the comparable size of reactors for both nonthermal plasma depolymerization and catalytic reactions, suggesting the feasibility of scaling up nonthermal depolymerization for upcycling of polymer wastes.

4. Conclusion

The results of this study provide compelling evidence for the efficacy of ambient nonthermal air plasma in the selective depolymerization of a specialty polymer – polyvinyl alcohol. One unique feature of our approach is the use of short pulses of AC power, avoiding the significant temperature rise commonly associated with nonthermal plasma processes. It should be emphasized that many reported nonthermal plasma processes were not operated with a short pulse of AC power, resulting in a significant rise in reactor temperature. We also found that oxygen in air plasma is essential for achieving high selectivity in the formation of aldehyde products from polyvinyl alcohol (PVA). The controlled selectivity in the oxidation of polyvinyl alcohol (PVA) can be achieved by varying polymer-to-TiO₂ ratios. The significant formation of propionaldehyde, not previously reported in nonthermal plasma reactions, unveils an unprecedented reaction pathway for the direct conversion of C-OH to CH₃. We plan to further test this step for small alcohol, diol, polyol molecules. This finding not only enriches our understanding of plasma chemistry but also highlights the potential for direct conversion of specific functional groups in polymers in an oxidative environment at ambient temperature.

The selectivity levels for aldehydes and CO₂ can be manipulated by the nitrogen to oxygen ratio in plasma and TiO₂, respectively, further demonstrating the versatility of this approach. In situ IR study is being planned to investigate the specific role of TiO₂ catalyst. This research lays the groundwork for future studies to explore the broader

applicability of this technology in polymer waste management and the synthesis of small, valuable molecules with and without catalysts, potentially revolutionizing material recycling process-based chemistry at ambient temperature. The study also showed the transient approach by introducing a perturbation, applying a pulse of AC power, is highly effective in gaining molecular level understanding of the role of diffusion and re-adsorption in reaction system, including nonthermal plasma reaction.

In conclusion, the ambient nonthermal air plasma research could not only contribute to the field of plasma and catalytic chemistry but also offers a promising avenue for addressing the global challenge of polymer waste, highlighting the potential for such innovative technologies to make substantial contributions to sustainable development and circular economy initiatives.

CRediT authorship contribution statement

Aderinsola Oduntan: Data curation, Formal analysis, Investigation, Writing – review & editing. **Jingfan Wei:** Data curation. **Jiayang Ma:** Data curation. **Anthony Toskin:** Formal analysis. **Toshikazu Miyoshi:** Writing – review & editing, Supervision. **Tianbo Liu:** Supervision, Writing – review & editing. **Steven S.C. Chuang:** Funding acquisition, Conceptualization, Methodology, Supervision, Writing – original draft, Writing – review & editing.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Steven S.C Chuang reports financial support was provided by National Science Foundation. If there are other authors, they declare that

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

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.apcato.2024.206921>.

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